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(21) International Application Number: PCT/US99/00012 (22) International Filing Date: 4 January 1999 (04.01.99) (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): SAKO, Takashi [JP/JP]; 2-3-202, Uozakikitamachi 6-chome, Higashinada-ku, Kobe 658-0082 (JP). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).		(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: TRANSPARENT HAIR CONDITIONING COMPOSITION COMPRISING HYDROPHOBIC EMULSIFIER AND BREAKABLE VISIBLE PARTICLE (57) Abstract Disclosed is a hair conditioning composition comprising: (1) a hydrophobic emulsifier selected from the group consisting of carboxylic acid/carboxylate copolymer, nonionic surfactant having an HLB of from about 1 to 10, silicone derivative surfactant, and mixtures thereof; (2) a breakable visible particle comprising structural material selected from the group consisting of polysaccharides and their derivatives, saccharides and their derivatives, oligosaccharides, monosaccharides, and mixtures thereof; and (3) an oily continuous phase carrier; wherein the composition is transparent.		

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TRANSPARENT HAIR CONDITIONING COMPOSITION COMPRISING HYDROPHOBIC EMULSIFIER AND BREAKABLE VISIBLE PARTICLE

5

TECHNICAL FIELD

The present invention relates to hair conditioning compositions comprising
10 an hydrophobic emulsifier and a breakable visible particle in an oily continuous
phase carrier.

BACKGROUND

Human hair becomes soiled due to its contact with the surrounding
15 environment and from sebum secreted by the scalp. The soiling of the hair
causes it to have a dirty or greasy feel, and an unattractive appearance. The
soiling of the hair necessitates shampooing with regularity.

Shampooing cleans the hair by removing excess soil and sebum.
However, shampooing can leave the hair in a wet, tangled, and generally
20 unmanageable state. Once the hair dries, it is often left in a dry, rough, lusterless,
or frizzy condition due to removal of the hair's natural oils and other natural
conditioning and moisturizing components. The hair can further be left with
increased levels of static upon drying which can interfere with combing and result
in a condition commonly referred to as "fly-away hair", or contribute to an
25 undesirable phenomena of "split ends", particularly for long hair.

A variety of approaches have been developed to alleviate these after-
shampoo problems. These approaches range from post-shampoo application of
hair conditioner such as leave-on and rinse-off products, to hair conditioning
shampoos which attempt to both cleanse and condition the hair from a single
30 product. Although some consumers prefer the ease and convenience of a
shampoo which includes conditioners, a substantial proportion of consumers
prefer the more conventional conditioner formulations which are applied to the
hair as a separate step from shampooing, usually subsequent to shampooing.
Such consumers who prefer the conventional conditioner formulations value the
35 relatively higher conditioning effect, or convenience of changing the amount of
conditioning depending on the condition of hair or portion of hair.

Conditioning formulations can be in the form of rinse-off products or leave-on products, and can be in the form of an emulsion, cream, gel, spray, and mousse. Products in the form of cream, gel, and mousse are suitable in that the consumer can easily control the amount and distribution of the product. As such, these products are particularly suitable for leave-on products.

Leave-on products having aesthetic advantages are preferred by the consumer. Transparent or nearly transparent products including distinct visible particles are particularly preferred with regard to aesthetics. Such visible particles are also useful in encompassing materials which may affect the stability of the base formula. However, conventional leave-on products are not completely satisfactory in providing such aesthetic effects while delivering good conditioning benefits.

Based on the foregoing, there remains a desire to provide hair conditioning compositions suitable for leave-on use which provide favorable aesthetic benefits, and are compatible with a wide range of additional conditioning agents.

None of the existing art provides all of the advantages and benefits of the present invention.

SUMMARY

The present invention is directed to a hair conditioning composition comprising:

- (1) a hydrophobic emulsifier selected from the group consisting of carboxylic acid/carboxylate copolymer, nonionic surfactant having an HLB of from about 1 to about 10, silicone derivative surfactant, and mixtures thereof;
- (2) a breakable visible particle comprising structural material selected from the group consisting of polysaccharides and their derivatives, saccharides and their derivatives, oligosaccharides, monosaccharides, and mixtures thereof; and

- (3) an oily continuous phase carrier;

wherein the composition is transparent.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

DETAILED DESCRIPTION

While the specification concludes with claims which particularly point out and distinctly claim the invention, it is believed the present invention will be better understood from the following description.

5 All cited references are incorporated herein by reference in their entireties. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

Herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms
10 "consisting of" and "consisting essentially of".

All percentages, parts and ratios are based upon the total weight of the compositions of the present invention, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and, therefore, do not include carriers or by-products that may be included in
15 commercially available materials.

The aspects and embodiments of the present invention set forth in this document have many advantages. For example, the hair conditioning compositions of the present invention provide: improved conditioning benefits to the hair such as smoothness, softness, and reduction of friction, are easy to
20 apply on the hair, and leave the hair and hands with a clean feeling. In one embodiment of the present invention, a transparent hair conditioning composition can be provided.

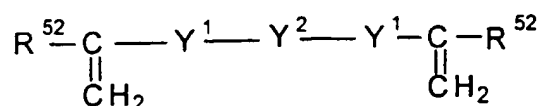
HYDROPHOBIC EMULSIFIER

The compositions of the present invention comprise a hydrophobic
25 emulsifier selected from the group consisting of carboxylic acid/carboxylate copolymers, nonionic surfactant having an HLB of from about 1 to about 10, silicone derivative surfactant, and mixtures thereof. These hydrophobic emulsifiers herein are soluble or miscible with the oily continuous phase carrier, and have the ability to increase the viscosity of the composition. In a preferred
30 embodiment, the hydrophobic emulsifier is selected so that the composition of the present composition has a suitable viscosity, preferably from about 1,000 cps to about 100,000 cps, more preferably from about 2,000 cps to about 50,000cps. If such a viscosity is not achieved, additional conditioning agent which contribute to viscosity building may be added. The viscosity herein can be suitably
35 measured by Brookfield RVT at 20rpm at 20°C using either spindle #4, 5, 6 or 7

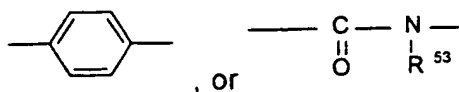
depending on the viscosity and the characteristic of the composition. The hydrophobic emulsifiers herein are preferably used at levels by weight of the composition of from about 0.001% to about 20%, more preferably from about 0.05% to about 10%.

5 Carboxylic Acid/Carboxylate Copolymer

The carboxylic acid/carboxylate copolymers herein are hydrophobically-modified cross-linked copolymers of carboxylic acid and alkyl carboxylate, and have an amphiphilic property. These carboxylic acid/carboxylate copolymers are obtained by copolymerizing 1) a carboxylic acid monomer such as acrylic acid,
10 methacrylic acid, maleic acid, maleic anhydride, itaconic acid, fumaric acid, crotonic acid, or α -chloroacrylic acid, 2) a carboxylic ester having an alkyl chain of from 1 to about 30 carbons, and preferably 3) a crosslinking agent of the following formula:



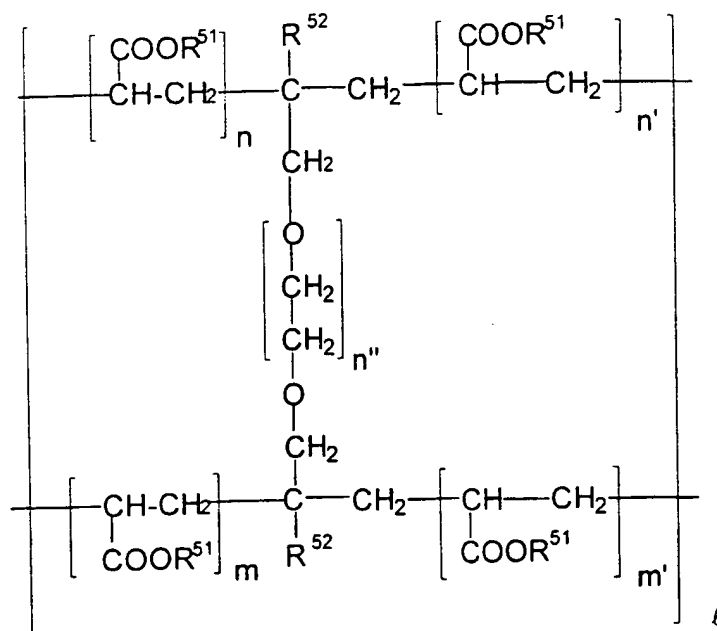
15 wherein R^{52} is a hydrogen or an alkyl group having from about 1 to about 30 carbons; Y^1 , independently, is oxygen, CH_2O , COO , OCO ,



, wherein R^{53} is a hydrogen or an alkyl group having from about 1 to about 30 carbons; and Y^2 is selected from $(\text{CH}_2)_{m''}$,
20 $(\text{CH}_2\text{CH}_2\text{O})_{m''}$, or $(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_{m''}$ wherein m'' is an integer of from 1 to about 30. The carboxylic acid/carboxylate copolymers herein are believed to provide appropriate viscosity and rheology properties to the composition, and to emulsify and stabilize certain conditioning agents in the composition. It is further
25 believed that, because of the alkyl group contained in the copolymer, the carboxylic acid/carboxylate copolymers do not make the composition undesirably sticky.

The composition of the present invention preferably comprises the carboxylic acid/carboxylate copolymer at a level by weight of from about 0.01% to about 10%, more preferably from about 0.1% to about 2%.

30 Suitable carboxylic acid/carboxylate copolymers herein are acrylic acid/alkyl acrylate copolymers having the following formula:



wherein R^{51} , independently, is a hydrogen or an alkyl of 1 to 30 carbons wherein at least one of R^{51} is a hydrogen, R^{52} is as defined above, n , n' , m and m' are integers in which $n+n'+m+m'$ is from about 40 to about 100, n'' is an integer of from 1 to about 30, and ℓ is defined so that the copolymer has a molecular weight of about 500,000 to about 3,000,000.

Commercially available carboxylic acid/carboxylate copolymers useful herein include: CTFA name Acrylates/C10-30 Alkyl Acrylate Crosspolymer having tradenames Pemulene TR-1, Pemulene TR-2, Carbopol 1342, Carbopol 1382, and Carbopol ETD 2020, all available from B. F. Goodrich Company.

Neutralizing agents may be included to neutralize the carboxylic acid/carboxylate copolymers herein. Nonlimiting examples of such neutralizing agents include sodium hydroxide, potassium hydroxide, ammonium hydroxide, monethanolamine, diethanolamine, triethanolamine, diisopropanolamine, aminomethylpropanol, tromethamine, tetrahydroxypropyl ethylenediamine, and mixtures thereof.

Nonionic Surfactant

The nonionic surfactants herein are those having an HLB of from about 1 to about 10, preferably from about 5 to about 8, and mixtures thereof.

Useful herein are polyol esters such as POE(2) nonylphenyl ether, POE(5) nonylphenyl ether and POE octylphenyl ether, POE(2) cetyl ether,

POE(2) stearyl ether, POE(2) oleyl ether and POE(5) behenyl ether, and POE(1)POP(8)cetyl ether.

Useful herein are polyethyleneglycol fatty acid ethers such as ethyleneglycol (2EO, 4EO) monostearate and polyethyleneglycol (2EO) monooleate.

Useful herein are polyoxyethylene castor oil such as POE(3) castor oil, POE(10) castor oil, POE(5) hydrogenated castor oil and POE(10) hydrogenated castor oil.

Useful herein are polyglycerin fatty acid ethers such as diglyceryl monostearate, diglyceryl monooleate, diglyceryl dioleate, tetraglyceryl monostearate, tetraglyceryl monooleate, tetraglyceryl tristearate, hexaglyceryl tristearate, hexaglyceryl pentastearate, hexaglyceryl pentaoleate, decaglyceryl tristearate and decaglyceryl trioleate.

Useful herein are glycerin fatty acid ethers such as glyceryl monomyristate, glyceryl monostearate and glyceryl monooleate.

Useful herein is polyoxyethylene glycerin fatty acid ether such as POE(5) glyceryl monostearate.

Useful herein is propylene glycol fatty acid ether such as propylene glycol monostearate.

Useful herein are polyoxyethylene alkylamine such as POE(5) oleylamine and POE(4) stearylamine.

Useful herein are sorbitan esters such as sorbitan trioleate, sorbitan triisostearate, sorbitan tristearate, sorbitan sesquioleate, sorbitan oleate, sorbitan stearate, and sorbitan isostearate.

Useful herein are ethoxylated fatty alcohols such as cetareth-2, ceteth-2.

Useful herein are lanolin and its derivatives such as cholesterol, and lanolin alcohol.

Silicone Derivative Surfactant

The silicone derivative surfactants herein are those derived from organic siloxanes. Useful herein are polyoxyethylene methylpolysiloxane copolymer with CTFA name Dimethicone copolyol such as SH3746, SH3771C, SH3772C, SH3773C, SH3775C, SH3748 and SH3749 from Dow Corning.

BREAKABLE VISIBLE PARTICLE

The structural material provides a certain strength to the breakable visible particle so that they retain their distinctively detectable structure in the present

composition under normal shelf conditions, while they can be broken and disintegrated with very little shear on the hand with the fingers upon use. Preferably, the breakable visible particles have a compression strength of about 1 to about 200 grams per particle. Compression strength can be suitably measured with a batch of 20 particles using TA-XT2 Texture Analyzer supplied by Stable Micro Systems Ltd. under the following conditions:

Mode: Measure force in compression
Test speed: 0.1 mm/s
Distance: 0.8 mm
Trigger type: Auto - 10g
Accessory: 25mm cylinder probe (P/25) on acrylate resin plate using 5kg load cell

Further, after the breakable visible particles are disintegrated, they leave little to no residual feeling on the hand, preferably no fragment particles of more than about 10 μ m.

The structural material comprises components selected from the group consisting of polysaccharides and their derivatives, saccharides and their derivatives, oligosaccharides, monosaccharides, and mixtures thereof. Preferably, components having different water solubility are selected from the above mentioned group to make the structural material. More preferably, the structural material comprises components selected from the group consisting of cellulose, cellulose derivatives, saccharides, and mixtures thereof. Still preferably, the structural material comprises a mixture of cellulose, cellulose derivatives, and saccharides.

Exemplary components useful for making the structural material include: polysaccharide and saccharide derivatives such as crystalline cellulose, cellulose acetate, cellulose acetate butyrate, cellulose acetate phthalate, cellulose nitrate, ethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose, hydroxypropylmethylcellulose phthalate, methyl cellulose, sodium carboxymethylcellulose, gum acacia (gum arabic), agar, agarose, maltodextrin, sodium alginate, calcium alginate, dextran, starch, galactose, glucosamine, cyclodextrin, chitin, amylose, amylopectin, glycogen, laminaran, lichenan, curdlan, inulin, levan, pectin, mannan, xylan, alginic acid, arabic acid, glucomannan, agarose, agarpectin, prophyran, carrageenen, fucoidan, glycosaminoglycan, hyaluronic acid, chondroitin, peptidoglycan.

lipopolysaccharide, guar gum, starch, and starch derivatives; oligosaccharides such as sucrose, lactose, maltose, uronic acid, muramic acid, cellobiose, isomaltose, planteose, melezitose, gentianose, maltotriose, stachyose, glucoside and polyglucoside; monosaccharides such as glucose, fructose, and mannose.

5 Components which may further be comprised in the structural material include; synthetic polymers such as acrylic polymers and copolymers including polyacrylamide, poly(alkyl cyanoacrylate), and poly(ethylene-vinyl acetate), and carboxyvinyl polymer, polyamide, poly(methyl vinyl ether-maleic anhydride), poly(adipyl-L-lysine), polycarbonate, polyterephthalamide, polyvinyl acetate

10 phthalate, poly(terephthaloyl-L-lysine), polyarylsulfone, poly(methylmethacrylate), poly(ϵ -caprolactone), polyvinylpyrrolidone, polydimethylsiloxane, polyoxyethylene, polyester, polyglycolic acid, polylactic acid, polyglutamic acid, polylysine, polystyrene, poly(styrene-acrylonitrile), polyimide, and poly(vinyl alcohol); and other material such as fat, fatty acid, fatty alcohol, milk solids,

15 molasses, gelatin, gluten, albumin, shellac, caseinate, bees wax, carnauba wax, spermaceti wax, hydrogenated tallow, glycerol monopalmitate, glycerol dipalmitate, hydrogenated castor oil, glycerol monostearate, glycerol distearate, glycerol tristearate, 12-hydroxystearyl alcohol, protein, and protein derivatives; and mixtures thereof. Components herein may be described in other sections as

20 useful components for the present composition. The components herein, however, are substantially used to make the structure of the breakable visible particles, and are substantially not dissolved in the bulk of the present composition under normal shelf conditions.

Components which may further be comprised in the structural material

25 include; polysaccharide and saccharide derivatives such as crystalline cellulose, cellulose acetate, cellulose acetate butyrate, cellulose acetate phthalate, cellulose nitrate, ethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose, hydroxypropylmethylcellulose phthalate, methyl cellulose, sodium carboxymethylcellulose, gum acacia (gum arabic), agar,

30 agarose, maltodextrin, sodium alginate, calcium alginate, dextran, starch, galactose, glucosamine, cyclodextrin, chitin, amylose, amylopectin, glycogen, laminaran, lichenan, curdlan, inulin, levan, pectin, mannan, xylan, alginic acid, arabic acid, glucommannan, agarose, agarpectin, prophyran, carrageenen, fucoidan, glycosaminoglycan, hyaluronic acid, chondroitin, peptidoglycan,

35 lipopolysaccharide, guar gum, starch, and starch derivatives; oligosaccharides

such as sucrose, lactose, maltose, uronic acid, muramic acid, cellobiose, isomaltose, planteose, melezitose, gentianose, maltotriose, stachyose, glucoside and polyglucoside; monosaccharides such as glucose, fructose, and mannose, and other material such as milk solids, molasses, gelatin, gluten, albumin, shellac, caseinate, bees wax, carnauba wax, spermaceti wax, hydrogenated tallow, glycerol monopalmitate, glycerol dipalmitate, hydrogenated castor oil, glycerol monostearate, glycerol distearate, glycerol tristearate, 12-hydroxystearyl alcohol, protein, and protein derivatives; and mixtures thereof. Components herein may be described in other sections as useful components for the present composition. The components herein, however, are substantially used to make the structure of the breakable visible particles, and are substantially not dissolved in the bulk of the present composition under normal shelf conditions.

The breakable visible particle herein may encompass, contain, or be filled with an encompassed material. Such encompassed material can be water soluble or water insoluble, and comprise components such as: vitamins, antioxidants, refreshing agents, proteins and protein derivatives, herbal extracts, pigments, dyes, antimicrobial agents, chelating agents, UV absorbers, optical brighteners, silicone compounds, perfumes, humectants which are generally water soluble, additional conditioning agents which are generally water insoluble, and mixtures thereof. In one embodiment, water insoluble components are preferred encompassed material. In such an embodiment, silicone compounds which are non-volatile can be used as coating material to the breakable visible particle to avoid leakage of the encompassed material into the bulk of the composition.

VITAMINS AND AMINO ACIDS

Vitamins and amino acids useful as encompassed material herein include: water soluble vitamins such as vitamin B1, B2, B6, B12, C, pantothenic acid, pantothenyl ethyl ether, panthenol, biotin, and their derivatives, water soluble amino acids such as asparagine, alanin, indole, glutamic acid and their salts, water insoluble vitamins such as vitamin A, D, E, and their derivatives, water insoluble amino acids such as tyrosine, tryptamine, and their salts.

ANTIOXIDANTS

Antioxidants useful as encompassed material herein include: sesamol, sesamolin, gossypol, BHA (butyl hydroxy anisole, BHT (dibutyl hydroxy toluene), nordihydroguaiaretic acid, propyl gallate, phytic acid, and guajacum resin.

Synergists for these antioxidants may be included; such as citric acid, ascorbic acid, and malic acid.

REFRESHING AGENTS

Refreshing agents useful as encompassed material herein include
5 menthol and camphor in their d- and dl- forms.

PIGMENTS

Pigments useful as encompassed material herein include inorganic, nitroso, monoazo, disazo, carotenoid, triphenyl methan, triaryl methane, xanthene, quinoline, oxazine, azine, anthraquinone, indigoid, thionindigoid,
10 quinacridone, phthalocianine, botanical, natural colors, including: water soluble components such as those having C. I. Names: Acid Red 18, 26, 27, 33, 51, 52, 87, 88, 92, 94, 95, Acid Yellow 1, 3, 11, 23, 36, 40, 73, Food Yellow 3, Food Green 3, Food blue 2, Food Red 1, 6, Acid Blue 5, 9, 74, Pigment Red 57-1, 53(Na), Basic Violet 10, Solvent Red 49, Acid orange 7, 20, 24, Acid Green 1, 3,
15 5, 25, Solvent Green 7, Acid Violet 9, 43; water insoluble components such as those having C. I. Names: Pigment Red 53(Ba), 49(Na), 49(Ca), 49(Ba), 49(Sr), 57, Solvent Red 23, 24, 43, 48, 72, 73, Solvent Orange 2, 7, Pigment Red 4, 24, 48, 63(Ca)3, 64, Vat Red 1, Vat blue 1, 6, Pigment Orange 1, 5, 13, Solvent Yellow 5, 6, 33, Pigment Yellow 1, 12, Solvent Green 3, Solvent Violet 13,
20 Solvent Blue 63, Pigment Blue 15, titanium dioxides, chlorophyllin copper complex, ultramarines, aluminum powder, bentonite, calcium carbonate, barium sulfate, bismuthine, calcium sulfate, carbon black, bone black, chromic acid, cobalt blue, gold, ferric oxides, hydrated ferric oxide, ferric ferrocyanide, magnesium carbonate, manganous phosphate, silver, and zinc oxides.

ANTIMICROBIAL AGENTS

Antimicrobial agents useful as encompassed material include those useful
as cosmetic biocides and antidandruff agents anti-itchiness agents including:
water soluble components such as piroctone olamine, water insoluble
components such as 3,4,4'- trichlorocarbanilide (trichlosan), triclocarban, zinc
30 pyrithione, selenium disulfide, alkylisoquinolinium bromide, biphenamine, thianthol, cantharides tincture, ginger tincture, and capsicum tincture.

CHELATING AGENTS

Chelating agents useful as encompassed material include: 2,2'-
dipyridylamine; 1,10-phenanthroline {o-phenanthroline}; di-2-pyridyl ketone; 2,3-
35 bis(2-pyridyl) pyrazine; 2,3-bis(2-pyridyl)-5,6-dihydropyrazine; 1,1'-

carbonyldiimidazole; 2,4-bis(5,6-diphenyl-1,2,4-triazine-3-yl)pyridine; 2,4,6-tri(2-pyridyl)-1,3,5-triazine; 4,4'-dimethyl-2,2'-dipyridyl; 2,2'-biquinoline; di-2-pyridyl glyoxal {2,2'-pyridyl}; 2-(2-pyridyl)benzimidazole; 2,2'-bipyrazine; 3-(2-pyridyl)5,6-diphenyl-1,2,4-triazine; 3-(4-phenyl-2-pyridyl)-5-phenyl-1,2,4-triazine; 3-(4-phenyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine; 2,3,5,6-tetrakis-(2'-pyridyl)-pyrazine; 2,6-pyridinedicarboxylic acid; 2,4,5-trihydroxypyrimidine; phenyl 2-pyridyl ketoxime; 3-amino-5,6-dimethyl-1,2,4-triazine; 6-hydroxy-2-phenyl-3(2H)-pyridazinone; 2,4-pteridinediol {lumazine}; 2,2'-dipyridyl; and 2,3-dihydroxypyridine.

UV ABSORBER

UV absorbers useful as encompassed material herein can be water soluble or water insoluble, including: p-aminobenzoic acid, its salts and its derivatives (ethyl, isobutyl, glyceryl esters; p-dimethylaminobenzoic acid); anhranilates (i.e., o-aminobenzoates; methyl, menthyl, phenyl, benzyl, phenylethyl, linalyl, terpinyl, and cyclohexenyl esters); salicylates (amyl, phenyl, benzyl, menthyl, glyceryl, and dipropylene glycol esters); cinnamic acid derivatives (menthyl and benzyl esters, -phenyl cinnamionitrile; butyl cinnamoyl pyruvate; trihydroxycinnamic acid derivatives (esculetin, methylesculetin, daphnetin, and the glucosides, esculin and daphnin); dibenzalacetone and benzalacetophenone; naphtholsulfonates (sodium salts of 2-naphthol-3,6-disulfonic and of 2-naphthol-6,8-disulfonic acids); dihydroxy-naphthoic acid and its salts; o- and p-Hydroxybiphenyldisulfonates; quinine salts (bisulfate, sulfate, chloride, oleate, and tannate); quinoline derivatives (8-hydroxyquinoline salts, 2-phenylquinoline); hydroxy- or methoxy-substituted benzophenones; uric and vilouric acids; tannic acid and its derivatives (e.g., hexaethylether); (butyl carbityl) (6-propyl piperonyl) ether; hydroquinone; benzophenones (oxybenzene, sulisobenzene, dioxybenzene, benzoescorcinol, 2,2',4,4'-Tetrahydroxybenzophenone, 2,2'-Dihydroxy-4,4'-dimethoxybenzophenone, octabenzene); 4-Isopropylidibenzoylmethane; butylmethoxydibenzoylmethane; etocrylene; and 4-isopropyl-di-benzoylmethane. Of these, 2-ethylhexyl p-methoxycinnamate, 4,4'-t-butyl methoxydibenzoylmethane, 2-hydroxy-4-methoxybenzophenone, octyldimethyl p-aminobenzoic acid, digalloyltriolate, 2,2-dihydroxy-4-methoxybenzophenone ethyl 4-[bis(hydroxypropyl)]aminobenzoate, 2-ethylhexyl 2-cyano-3,3-diphenylacrylate, 2-ethylhexylsalicylate, glyceryl p-aminobenzoate, 3,3,5-trimethylcyclohexylsalicylate, methylanthranilate, p-dimethyl-aminobenzoic acid

or aminobenzoate, 2-ethylhexyl p-dimethylamino-benzoate, 2-phenylbenzimidazole-5-sulfonic acid, 2-(p-dimethylaminophenyl)-5-sulfonicbenzoxazoic acid and mixtures thereof. Preferred sunscreens useful in the compositions of the present invention are 2-ethylhexyl p-methoxycinnamate, butylmethoxydibenzoylmethane, 2-hydroxy-4-methoxybenzophenone, octyldimethyl p-aminobenzoic acid and mixtures thereof.

OPTICAL BRIGHTENER

Optical brighteners useful as encompassed material herein include compounds which absorb ultraviolet light and re-emit the energy in the form of visible light. Specifically, the optical brighteners useful herein have an absorption, preferably a major absorption peak, between a wavelength of about 1nm and about 420nm, and an emission, preferably a major emission peak, between a wavelength of about 360nm and about 830nm; wherein the major absorption peak has a shorter wavelength than the major emission peak. More preferably, the optical brighteners useful herein have a major absorption peak between a wavelength of about 200nm and about 420nm, and a major emission peak between a wavelength of about 400nm and about 780nm. Optical brighteners may or may not have minor absorption peaks in the visible range between a wavelength of about 360nm and about 830nm. Optical brighteners can be described by other names in the art and in other industries, such as fluorescent whitening agents, fluorescent brighteners, and fluorescent dyes.

When applied to hair via suitable vehicles, optical brighteners herein provide benefits to the hair in three areas. First, optical brighteners herein alter the color of the hair by emitting light in the visible range. Second, optical brighteners herein enhance the shine of the hair by emitting light in the visible range. Third, optical brighteners herein protect the hair from ultraviolet light by absorbing ultraviolet light.

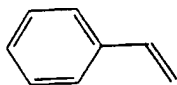
Optical brighteners in general are based on the structures of aromatic and heteroaromatic systems which provide these unique characteristics. The optical brighteners useful in the present invention can be water soluble and water insoluble, and can be classified according to their base structures, as described hereafter. Preferable optical brighteners herein include polystyrylstilbenes, triazinstilbenes, hydroxycoumarins, aminocoumarins, triazoles, pyrazolines, oxazoles, pyrenes, porphyrins, and imidazoles.

The optical brighteners useful herein are preferably used at levels by

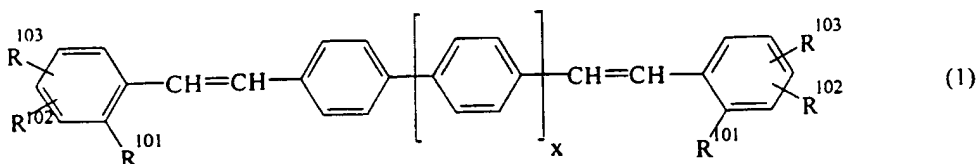
weight of the composition of from about 0.001% to about 10%.

Polystyrylstilbenes

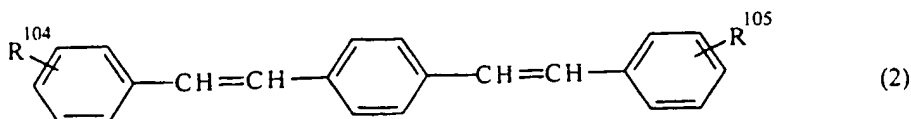
Polystyrylstilbenes are a class of compounds having two or more of the following base structure:



Polystyrylstilbenes useful in the present invention include those having formulae (1), (2) and (3):

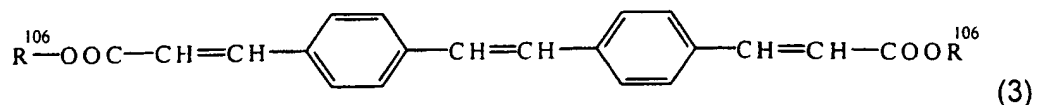


wherein R^{101} is H, OH, SO_3M , $COOM$, OSO_3M , $OPO(OH)OM$, wherein M is H, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra- C_1 - C_{30} -alkylammonium, mono-, di- or tri- C_1 - C_{30} -hydroxyalkylammonium or ammonium that is di- or tri-substituted with by a mixture of C_1 - C_{30} -alkyl and C_1 - C_{30} -hydroxyalkyl groups; or $SO_2N(C_1-C_{30}\text{-alkyl})_2$, $O-(C_1-C_{30}\text{-alkyl})$, CN, Cl, $COO(C_1-C_{30}\text{-alkyl})$, $CON(C_1-C_{30}\text{-alkyl})_2$ or $O(CH_2)_3N^+(CH_3)_2X^-$ wherein X^- is an anion of a chloride, bromide, iodide, formate, acetate, propionate, glycolate, lactate, acrylate, methanephosphonate, phosphite, dimethyl or diethyl phosphite anion; CN, or alkyl of 1 to 30 carbons, R^{102} and R^{103} , independently, are H, SO_3M wherein M is as previously defined; and x is 0 or 1; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably x is 1, R^{101} is SO_3Na and R^{102} and R^{103} are H; wherein the compound has a trans-coplanar orientation;



wherein R^{104} and R^{105} , independently, are CN, $COO(C_1-C_{30}\text{-alkyl})$, $CONHC_1$ -

C₄-alkyl, or CON(C₁-C₄-alkyl)₂, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R¹⁰⁴ and R¹⁰⁵ is 2-cyano, wherein the compound has a trans-coplanar orientation; and



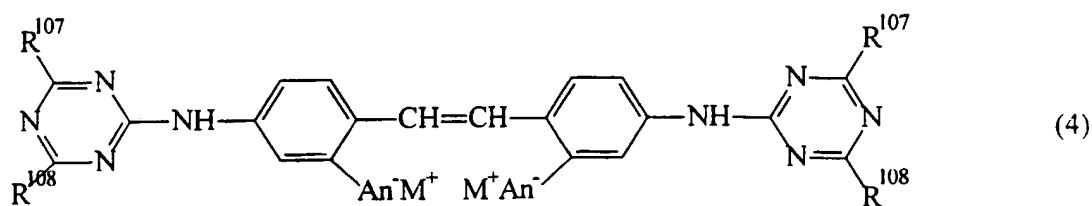
wherein each R¹⁰⁶, independently, is H, or alkyl of 1 to 30 carbons; and wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation.

Suitable polystyrylstilbenes include disodium-1, 4'-bis(2-sulfostyryl) bisphenyl (C.I. Fluorescent Brightener 351) with tradename Tinopal CBS-X available from Ciba Specialty Chemicals, 1,4-bis(2-cyanostyryl)benzene (C.I. Fluorescent Brightener 199) with tradename Ultraphor RN available from BASF.

Triazinstilbenes

Triazinstilbenes are a class of compounds having both triazin and stilbene structures in the same molecule.

Triazinstilbenes useful in the present invention include those having formulae (4):



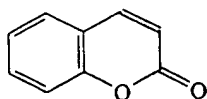
wherein R¹⁰⁷ and R¹⁰⁸, independently, are phenylamino, mono- or disulfonated phenylamino, morpholino, N(CH₂CH₂OH)₂, N(CH₃)(CH₂CH₂OH), NH₂, N(C₁-C₄-alkyl)₂, OCH₃, Cl, NH-(CH₂)₁₋₄SO₃H or NH-(CH₂)₁₋₄OH; An⁻ is an anion of a carboxylate, sulfate, sulfonate, or phosphate, and M is as previously defined, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R¹⁰⁷ is 2, 5-disulfophenylamino and each R¹⁰⁸ is morpholino; or each R¹⁰⁷ is 2, 5-disulfophenylamino and each R¹⁰⁸ is N(C₂H₅)₂; or each R¹⁰⁷ is 3-sulfophenyl and each R¹⁰⁸ is NH(CH₂CH₂OH) or N(CH₂CH₂OH)₂; or each R¹⁰⁷ is 4-sulfophenyl and each R¹⁰⁸ is

$N(CH_2CH_2OH)_2$; and in each case, the sulfo group is SO_3M in which M is sodium; wherein the compound has a trans-coplanar orientation.

Suitable triazinstilbenes include 4,4'-bis-[(4-anilino-6-bis(2-hydroxyethyl)amino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid with tradename Tinopal UNPA-GX available from Ciba Specialty Chemicals, 4,4'-bis-[(4-anilino-6-morpholine-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate with tradename Tinopal AMS-GX available from Ciba Specialty Chemicals, 4,4'-bis-[(4-anilino-6-(2-hydroxyethyl)methyl amino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate with tradename Tinopal 5BM-GX available from Ciba Specialty Chemicals, 4,4'-bis-[(4,6-dianilino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate, 4,4'-bis-[(4-anilino-6-methylamino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate, 4,4'-bis-[(4-anilino-6-ethylamino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate, and 4,4'-bis(4-phenyl-1,2,3-triazol-2-yl)stilbene-2,2'-disulfonic acid.

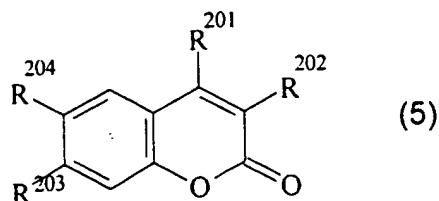
15 Hydroxycoumarins

Hydroxycoumarins are a class of compounds having the following base coumarin structure and having at least one hydroxy moiety:



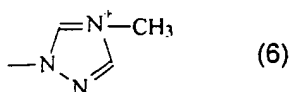
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Hydroxycoumarins useful in the present invention include those having formulae (5):

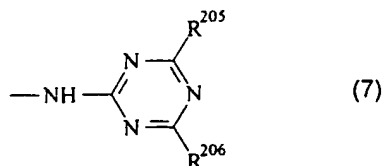


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wherein R^{201} is H, OH, Cl, CH_3 , CH_2COOH , CH_2SO_3H , CH_2OSO_3H , or $CH_2OPO(OH)OH$, R^{202} is H, phenyl, $COO-C_1-C_{30}$ -alkyl, glucose, or a group of formula (6):



and R²⁰³ is OH, or O-C₁-C₃₀-alkyl, and R²⁰⁴ is OH or O-C₁-C₃₀ alkyl, glycoside, or a group of the following formula (7):



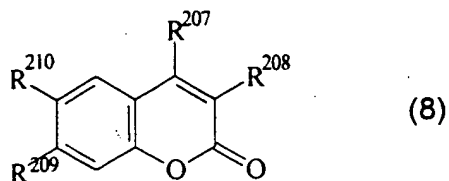
wherein R²⁰⁵ and R²⁰⁶ are independently, phenylamino, mono- or disulfonated phenylamino, morpholino, N(CH₂CH₂OH)₂, N(CH₃)(CH₂CH₂OH), NH₂, N(C₁-C₃₀-alkyl)₂, OCH₃, Cl, NH-(CH₂)₁₋₄SO₃H or NH-(CH₂)₁₋₄OH.

Suitable hydroxycoumarins include 6,7-dihydroxycoumarin available from Wako Chemicals, 4-methyl-7-hydroxycoumarin available from Wako Chemicals, 4-methyl-6,7-dihydroxycoumarin available from Wako Chemicals, esculin available from Wako Chemicals, and umbelliferone (4-hydroxycoumarin) available from Wako Chemicals.

Aminocoumarins

Aminocoumarins are a class of compounds having the base coumarin structure and having at least one amino moiety.

Aminocoumarins useful in the present inventions include those having formulae (8):



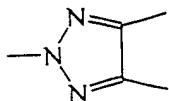
wherein R²⁰⁷ is H, Cl, CH₃, CH₂COOH, CH₂SO₃H, CH₂OSO₃H, or CH₂OPO(OH)OH, R²⁰⁸ is H, phenyl, or COOC₁-C₃₀ alkyl, and R²⁰⁹ and R²¹⁰ are independently H, NH₂, N(C₁-C₃₀alkyl)₂, NHC₁-C₃₀alkyl, or NHCOC₁-C₃₀alkyl.

Suitable aminocoumarins include 4-methyl-7,7'-diethylamino coumarin

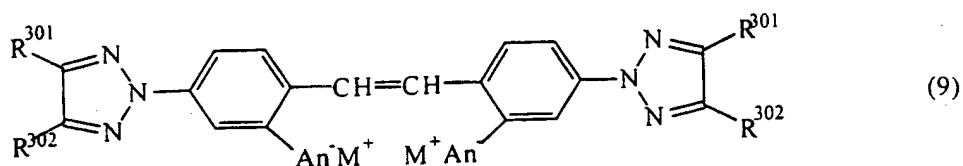
with tradename Calcofluor-RWP available from BASF, 4-methyl-7,7'-dimethylamino coumarin with tradename Calcofluor-LD available from BASF.

Triazoles

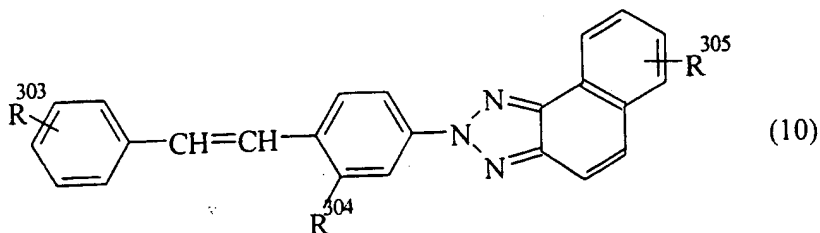
Triazoles are a class of compounds having the following base structure:



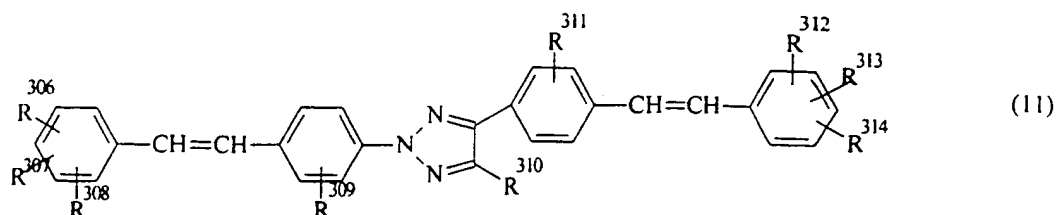
Triazoles useful in the present inventions include those having formulae (9) through (12) and (15) through (20):



wherein R³⁰¹ and R³⁰², independently, are H, C₁-C₃₀alkyl, phenyl or monosulfonated phenyl; An⁻ and M are as previously defined, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R³⁰¹ is phenyl, R³⁰² is H and M is sodium; wherein the compound has a trans-coplanar orientation;

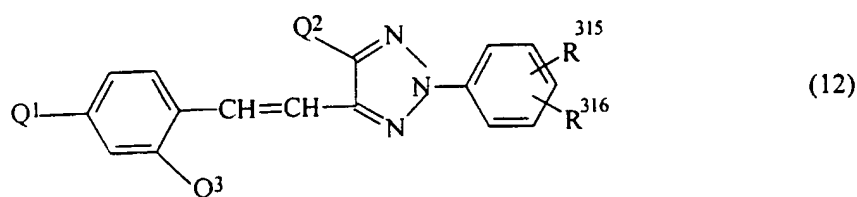


wherein R³⁰³ is H or Cl; R³⁰⁴ is SO₃M, SO₂N(C₁-C₃₀-alkyl)₂, SO₂O-phenyl or CN; R³⁰⁵ is H, SO₃M, COOM, OSO₃M, or OPO(OH)OM; and M is as previously defined, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R³⁰³ and R³⁰⁵ are H and R³⁰⁴ is SO₃M in which M is Na; wherein the compound has a trans-coplanar orientation;



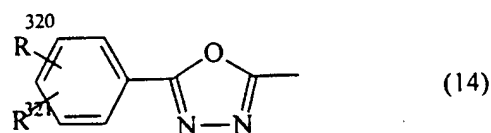
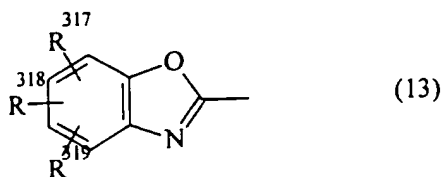
- wherein each of R³⁰⁶ and R³¹² independently represents H, a sulfonic acid group or the salts, esters or amides thereof, a carboxylic acid group or the salts, esters or amides thereof, a cyano group, a halogen atom, an unsubstituted or substituted alkylsulfonyl, arylsulfonyl, alkyl, alkoxy, aralkyl, aryl, aryloxy, aralkoxy or cycloalkyl radical, an unsubstituted or substituted 5-membered heterocyclic ring containing 2 to 3 nitrogen atoms or one oxygen atom and 1 or 2 nitrogen atoms, or together with R³⁰⁷ and R³¹³ they represent a methylenedioxy, ethylenedioxy, methylenoxymethylenoxy, trimethylene, tetramethylene, propenylene, butenylene or butadienylene radical, each of R³⁰⁷ and R³¹³ independently represents H, a sulfonic acid group or the salts, esters or amides thereof, a carboxylic acid group or the salts, esters or amides thereof, a cyano group, a halogen atom, an unsubstituted or substituted alkyl or alkoxy radical, or together with R³⁰⁶ and R³¹² represent a methylenedioxy, ethylenedioxy, methylenoxymethylenoxy, trimethylene, tetramethylene, propenylene, butenylene or butadienylene radical, each of R³⁰⁸ and R³¹⁴ independently represents H, a halogen atom or an unsubstituted or substituted alkyl radical, each of R³⁰⁹ and R³¹¹ independently represents H, a halogen atom, a cyano group a sulfonic acid group or the salts, esters or amides thereof, or a carboxylic acid group or the salts, esters or amides thereof, and R³¹⁰ independently represents H, a halogen atom, a cyano group a sulfonic acid group or the salts, alkyl radicals preferably by hydroxy, alkoxy of 1 to 30 carbon atoms, cyano, halogen, carboxy, sulfonic acid groups, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, phenyl or phenoxy; alkoxy radicals can be substituted by hydroxy, alkoxy of 1 to 30 carbon atoms, cyano, halogen, carboxy, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, phenyl or phenoxy; phenyl, phenylalkyl or phenoxy radicals can be substituted by halogen, cyano, carboxy, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, sulfo, or alkyl or alkoxy each of 1 to 30 carbon atoms; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; possible cycloalkyl radicals are preferably cyclohexyl and cyclopentyl radicals which can be substituted by alkyl of 1 to 30 carbon atoms; possible 5-

membered heterocyclic rings are v-triazole, oxazole or 1, 3, 4- oxdiazole radicals which can contain as substituents alkyl radicals of 1 to 4 carbon atoms, halogen, phenyl, carboxy, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, cyano, benzyl, alkoxy of 1 to 30 carbon atoms, phenoxy or sulfo, whilst two adjacent substituents of the triazole and oxazole radicals together are able to form a substituted or unsubstituted fused benzene nucleus; wherein the compound has a trans-coplanar orientation;



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wherein Q¹ denotes one of the ring systems (13) or (14);

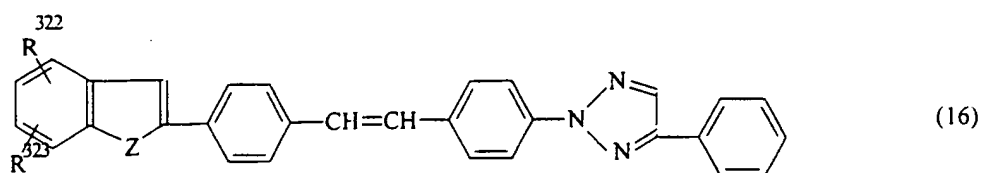
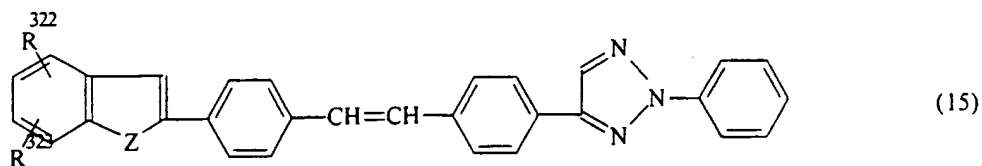


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and wherein R³¹⁷ denotes H, alkyl with 1 to 30 carbon atoms, cyclohexyl, phenylalkyl with C₁-C₃₀ carbon atoms in the alkyl part, phenyl, alkoxy with 1 to 30 carbon atoms, or Cl, or, conjointly with R³¹⁸, denotes alkylene with 3 to 30 carbon atoms, R³¹⁸ denotes H or alkyl with 1 to 30 carbon atoms or, conjointly with R³¹⁷, denotes alkylene with 3 to 30 carbon atoms, R³¹⁹ denotes H or methyl, R³²⁰ denotes H, alkyl with 1 to 30 carbon atoms, phenyl, alkoxy with 1 to 30 carbon atoms, or Cl, or, conjointly with R³²¹, denotes a fused benzene ring, R³²¹ denotes H or Cl or conjointly with R³²⁰, denotes a fused benzene ring, R³¹⁵ denotes H, alkyl with 1 to 30 carbon atoms, alkoxy with 1 to 30 carbon atoms or Cl, R³¹⁶ denotes H or Cl, Q² denotes H, Cl alkyl with 1 to 30 carbon atoms or phenyl and Q³ denotes H or Cl; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar

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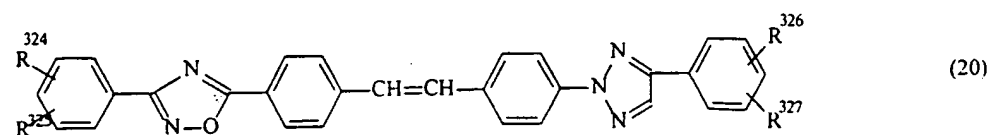
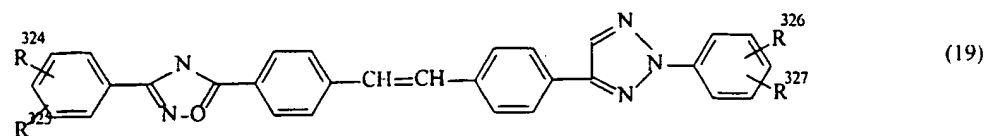
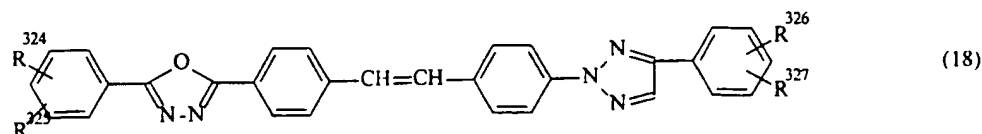
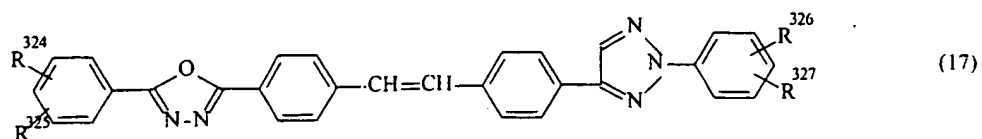
orientation;



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wherein R³²² denotes H, Cl, methyl, phenyl, benzyl, cyclohexyl or methoxy, R³²³ denotes H or methyl and Z denotes O or S; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation; and

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wherein R³²⁴ denotes H, Cl, alkyl with 1 to 30 carbon atoms, phenylalkyl with 1 to 30 carbon atoms, phenyl or alkoxy with 1 to 30 carbon atoms, or R³²⁴ conjointly with R³²⁵ denotes a fused benzene radical, R³²⁵ denotes H or methyl or R³²⁵ conjointly with R³²⁴ denotes a fused benzene radical, R³²⁶ denotes H, alkyl with 1 to 30 carbon atoms, alkoxy with 1 to 30 carbon atoms, Cl, carbalkoxy with 1 to 30 carbon atoms or alkylsulfonyl with 1 to 30 carbon atoms and R³²⁷

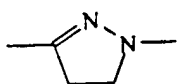
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denotes H, Cl, methyl or methoxy; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation.

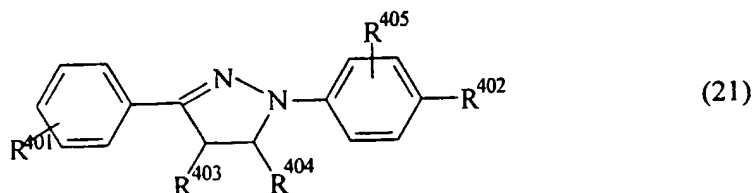
Suitable triazoles include 2-(4-styryl-3-sulfophenyl)-2H-naphtho[1,2-d]triazole (C.I. Fluorescent Brightener 46) with tradename Tinopal RBS available from Ciba Specialty Chemicals.

Pyrazolines

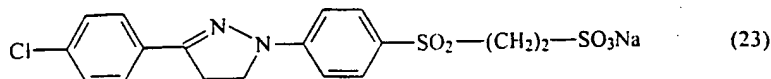
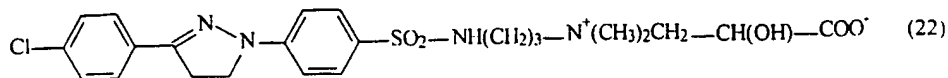
Pyrazolines are a class of compounds having the following base structure:



Pyrazolines useful in the present invention include those having formulae (21) through (23):



wherein R^{401} is H, Cl or $N(C_1-C_{30}\text{-alkyl})_2$, R^{402} is H, Cl, SO_3M , SO_2NH_2 , $SO_2NH-(C_1-C_{30}\text{alkyl})$, $COO-C_1-C_{30}\text{alkyl}$, $SO_2-C_1-C_{30}\text{alkyl}$, $SO_2NH(CH_2)_1-4N^+(CH_3)_3$ or $SO_2(CH_2)_1-4N^+H(C_1-C_{30}\text{-alkyl})_2An^-$, R^{403} and R^{404} are the same or different and each is H, $C_1-C_{30}\text{alkyl}$ or phenyl and R^{405} is H or Cl; and An^- and M are as previously defined, preferably R^{401} is Cl, R^{402} is $SO_2CH_2CH_2N^+H(C_1-C_4\text{-alkyl})_2An^-$ in which An^- is phosphite and R^{403} , R^{404} and R^{405} are each H; and formulae (22) and (23) shown below.

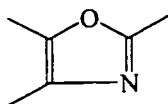


Suitable pyrazolines include 1-(4-amidosulfonylphenyl)-3-(4-chlorophenyl)-2-pyrazoline (C.I. Fluorescent Brightener 121) with tradename Blankophor DCB

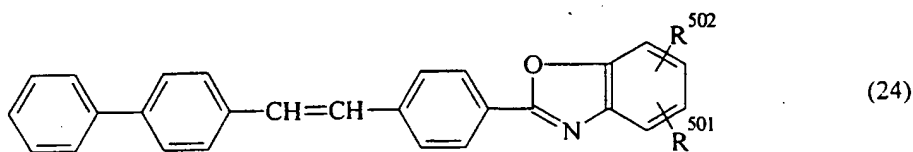
available from Bayer, 1-[4-(2-sulfoethylsulfonyl)phenyl]-3-(4-chlorophenyl)-2-pyrazoline, 1-[4-(2-sulfoethylsulfonyl)phenyl]-3-(3,4-dichloro-6-methylphenyl)-2-pyrazoline, 1-<4-{N-[3-(N,N,N-trimethylammonio)propyl]-amidodisulfonyl}phenyl>-3-(4-chlorophenyl)-2-pyrazoline methylsulfate, and 1-<4-{2-[1-methyl-2-(N,N-dimethylamino)ethoxy]ethylsulfonyl}phenyl>-3-(4-chlorophenyl)-2-pyrazoline methylsulfate.

Oxazoles

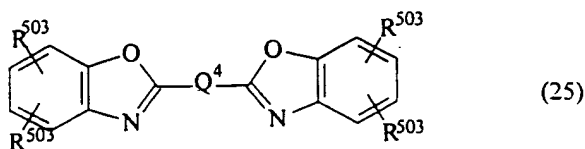
Oxazoles are a class of compounds having the following base structure:



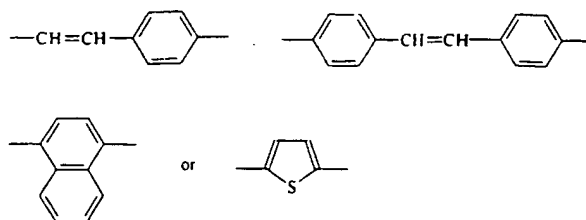
Oxazoles useful in the present inventions include those having formulae (24), (25), (26) and (27):



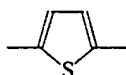
wherein R⁵⁰¹ and R⁵⁰², independently, are H, Cl, C₁-C₃₀alkyl or SO₂-C₁-C₃₀alkyl, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R⁵⁰¹ is 4-CH₃ and R⁵⁰² is 2-CH₃ wherein the compound has a trans-coplanar orientation;



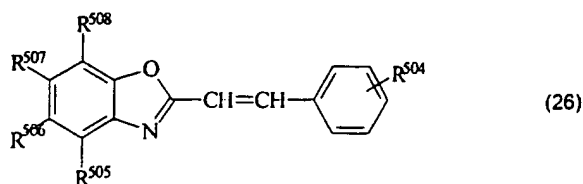
wherein R⁵⁰³, independently, is H, C(CH₃)₃, C(CH₃)₂-phenyl, C₁-C₃₀alkyl or COO-C₁-C₃₀alkyl, preferably H and Q⁴ is -CH=CH-;



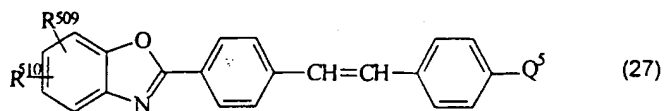
preferably



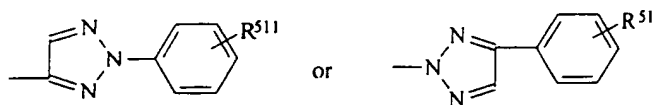
or one group R^{503} in each ring is 2-methyl and the other R^{503} is H and Q^4 is ---CH=CH--- ; or one group R^{503} in each ring is 2- $\text{C}(\text{CH}_3)_3$ and the other R^{503} is H; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation;



wherein R^{504} is CN, Cl, $\text{COO-C}_1\text{-C}_{30}$ alkyl or phenyl; R^{505} and R^{506} are the atoms required to form a fused benzene ring or R^{506} and R^{508} , independently, are H or $\text{C}_1\text{-C}_{30}$ alkyl; and R^{507} is H, $\text{C}_1\text{-C}_{30}$ alkyl or phenyl; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R^{504} is a 4-phenyl group and each of R^{505} to R^{508} is H; wherein the compound has a trans-coplanar orientation; and



wherein R^{509} denotes H, Cl, alkyl with 1 to 30 carbon atoms, cyclohexyl, phenylalkyl with 1 to 3 carbon atoms in the alkyl part, phenyl or alkoxy with 1 to 30 carbon atoms, R^{510} denotes H or alkyl with 1 to 30 carbon atoms, and Q^5 denotes a radical;

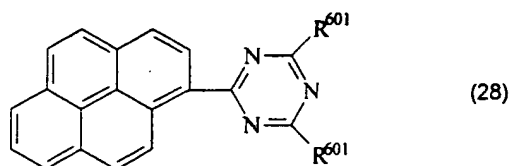


wherein R⁵¹¹ represents H, alkyl with 1 to 30 carbon atoms, alkoxy with 1 to 30 carbon atoms, Cl, carbalkoxy with 1 to 30 carbon atoms, unsubstituted sulfamoyl or sulfamoyl which is monosubstituted or disubstituted by alkyl or hydroxyalkyl with 1 to 30 carbon atoms or represents alkylsulfonyl with 1 to 30 carbon atoms; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation.

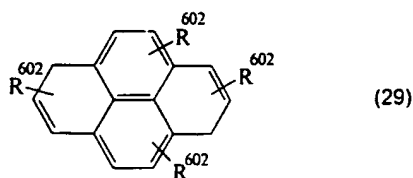
Suitable oxazoles include 4,4'-bis(5-methylbenzoxazol-2-yl)stilbene, and 2-(4-methoxycarbonylstyryl)benzoxazole.

Pyrenes

Pyrenes useful in the present invention include those having formulae (28) and (29):



wherein each R⁶⁰¹, independently, is C₁-C₃₀alkoxy; preferably methoxy; and



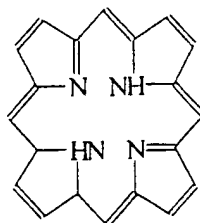
wherein each R⁶⁰², independently, is H, OH, or SO₃M, wherein M is as previously defined, sulfonated phenylamino, or anilino.

Suitable pyrenes include 2,4-dimethoxy-6-(1'-pyrenyl)-1,3,5-triazine (C.I. Fluorescent Brightener 179) with tradename Fluolite XMF, 8-hydroxy-1,3,6-pyrenetrisulfonic acid (D&C Green No.8), and 3-hydroxy-5,8,10-trisulphanilic pyrene.

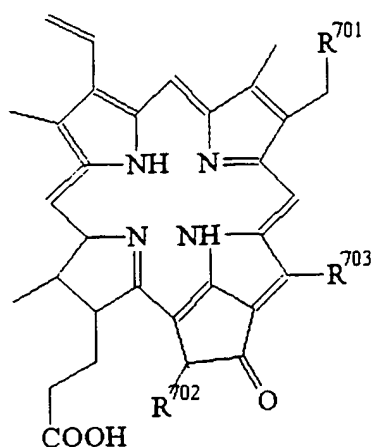
Porphyryns

Porphyryns useful in the present invention include those having formulae

(30), (31), and (32):

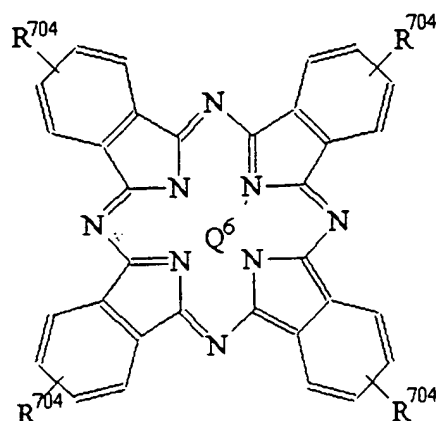


(30)



(31)

wherein R^{701} is CH_3 or CHO , R^{702} is H or $\text{COOC}_1\text{-C}_{30}$ alkyl, and R^{703} is H or an alkyl group having 1 to 30 carbons; and



(32)

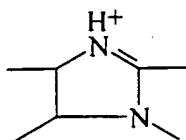
wherein each R^{704} , independently, is H , SO_3M , COOM , OSO_3M , or $\text{OPO}(\text{OH})\text{OM}$, wherein M is as previously defined, halide, or alkyl of 1 to 30

carbons; and Q⁶ is Cu, Mg, Fe, Cr, Co, or mixtures thereof with cationic charges.

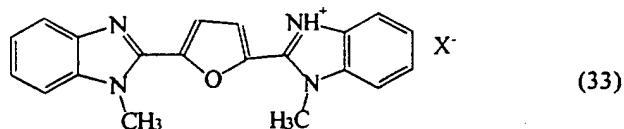
Suitable porphyrins include porphyrin available from Wako Chemicals and Copper II phthalocyanine available from Wako Chemicals.

Imidazoles

5 Imidazoles are a class of compounds having the following base structure:



10 Imidazoles useful in the present invention include those having formulae (33):



15 wherein X⁻ is as previously defined.

Suitable imidazoles include those with tradename of C.I. Fluorescence Brightener 352, or Uvtext AT available from Ciba Speciality Chemical.

HERBAL EXTRACT

20 Herbal extracts useful as encompassed material herein include those which are water soluble and those which are water insoluble. Useful herbal extracts herein include: Polygonum multiflori Extract, Houltuynia cordate extract, Phellodendron Bark extract, melilot extract, white dead nettle extract, licorice root extract, herbaceous peony extract, soapwort extract, dishcloth gourd extract, cinchona extract, creeping saxifrage extract, Sophora angustifolia extract, candock extract, common fennel extract, primrose extract, rose extract, 25 Rehmannia glutinosa extract, lemon extract, shikon extract, aloe extract, iris bulb extract, eucalyptus extract, field horsetail extract, sage extract, thyme extract, tea extract, laver extract, cucumber extract, clove extract, raspberry extract, melissa extract, ginseng extract, carrot extract, horse chestnut extract, peach extract, peach leaf extract, mulberry extract, cornflower extract, hamamelis extract, 30 placenta extract, thymus extract, silk extract, algae extract, althea extract, angelica dahurica extract, apple extract, apricot kernel extract, arnica extract,

Artemisia capillaris extract, astragal extract, balm mint extract, perilla extract, birch bark extract, bitter orange peel extract, Thea sinensis extract, burdock root extract, burnet extract, butcherbroom extract, Stephania cepharantha extract, matricaria extract, chrysanthemum flower extract, citrus unshiu peel extract, 5 cnidium extract, coix seed extract, coltsfoot extract, comfrey leaf extract, crataegus extract, evening primrose oil, gambir extract, ganoderma extract, gardenia extract, gentian extract, geranium extract, ginkgo extract, grape leaf extract, crataegus extract, henna extract, honeysuckle extract, honeysuckle flower extract, hoelen extract, hops extract, horsetail extract, hydrangea extract, 10 hypericum extract, isodonis extract, ivy extract, Japanese angelica extract, Japanese coptis extract, juniper extract, jujube extract, lady's mantle extract, lavender extract, lettuce extract, licorice extract, linden extract, lithospermum extract, loquat extract, luffa extract, malloti extract, mallow extract, calendula extract, moutan bark extract, mistletoe extract, mukurossi extract, mugwort 15 extract, mulberry root extract, nettle extract, nutmeg extract, orange extract, parsely extract, hydrolyzed conchiorin protein, peony root extract, peppermint extract, philodendron extract, pine cone extract, platycodon extract, polygonatum extract, rehmannia extract, rice bran extract, rhubarb extract, rose fruit extract, rosemary extract, royal jelly extract, safflower extract, saffron crocus extract, 20 sambucus extract, saponaria extract, Sasa albo marginata extract, Saxifraga stolonifera extract, scutellaria root extract, Cortinellus shiitake extract, lithospermum extract, sophora extract, laurel extract, calamus root extract, swertia extract, thyme extract, linden extract, tomato extract, turmeric extract, uncaria extract, watercress extract, logwood extract, grape extract, white lily 25 extract, rose hips extract, wild thyme extract, witch hazel extract, yarrow extract, yeast extract, yucca extract, zanthoxylum extract, and mixtures thereof.

Commercially available herbal extracts useful herein include Polygonum multiflori extracts which are water soluble, and available from Institute of Occupational Medicine, CAPM, China National Light Industry, and Maruzen, and 30 other herbal extracts listed above available from Maruzen.

Useful silicone compounds, humectants, and additional conditioning agents for encompassed material are the same as those exemplified in other portions of the specification. The components herein, however, are substantially retained within the breakable visible particles, and are substantially not dissolved 35 in the bulk of the present composition under normal shelf conditions.

Particularly useful commercially available breakable visible particles herein are those with tradenames Unisphere and Unicerin available from Induchem AG (Switzerland). Unisphere and Unicerin particles are made of microcrystalline cellulose, hydroxypropyl cellulose, lactose, vitamins, pigments, and proteins. Upon use, the Unisphere and Unicerin particles can be disintegrated with very little shear on the hand with the fingers with practically no resistance, and readily dissolve in the composition.

OILY CONTINUOUS PHASE CARRIER

The compositions of the present invention comprise an oily continuous phase carrier. By oily continuous phase carrier, what is meant is that the phase type is either oily or water-in-oil. The level and species of the carrier are selected according to the compatibility with other components, and other desired characteristic of the product.

The carrier is primarily made of oils having a melting point of less than about 25°C. These carrier oils can also provide conditioning benefit such as softness and flexibility to the hair. The carrier oils of this section are to be distinguished from the high melting point compounds described below. Nonlimiting examples of the carrier oils are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992.

The fatty alcohols useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated alcohols, preferably unsaturated alcohols. Nonlimiting examples of these compounds include oleyl alcohol, palmitoleic alcohol, isostearyl alcohol, isocetyl alcohol, undecanol, octyl dodecanol, octyl decanol, octyl alcohol, caprylic alcohol, decyl alcohol and lauryl alcohol.

The fatty acids useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Suitable fatty acids include, for example, oleic acid, linoleic acid, isostearic acid, linolenic acid, ethyl linolenic acid, arachidonic acid, and ricinolic acid.

The fatty acid derivatives and fatty alcohol derivatives are defined herein

to include, for example, esters of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, and bulky ester oils such as pentaerythritol ester oils, trimethylol ester oils, citrate ester oils, glyceryl ester oils, and mixtures thereof. Nonlimiting examples of fatty acid derivatives and fatty alcohol derivatives, include, for example, methyl linoleate, ethyl linoleate, isopropyl linoleate, isodecyl oleate, isopropyl oleate, ethyl oleate, octyldodecyl oleate, oleyl oleate, decyl oleate, butyl oleate, methyl oleate, octyldodecyl stearate, octyldodecyl isostearate, octyldodecyl isopalmitate, octyl isopelargonate, octyl pelargonate, hexyl isostearate, isopropyl isostearate, isodecyl isononanoate, isopropyl stearate, ethyl stearate, methyl stearate and Oleth-2. Bulky ester oils such as pentaerythritol ester oils, trimethylol ester oils, citrate ester oils and glyceryl ester oils useful herein are those which have a molecular weight of less than about 800, preferably less than about 500.

The hydrocarbons useful herein include straight chain, cyclic, and branched chain hydrocarbons which can be either saturated or unsaturated, so long as they have a melting point of not more than about 25°C. These hydrocarbons have from about 12 to about 40 carbon atoms, preferably from about 12 to about 30 carbon atoms, and preferably from about 12 to about 22 carbon atoms. Also encompassed herein are polymeric hydrocarbons of alkenyl monomers, such as polymers of C_{2-6} alkenyl monomers. These polymers can be straight or branched chain polymers. The straight chain polymers will typically be relatively short in length, having a total number of carbon atoms as described above. The branched chain polymers can have substantially higher chain lengths. The number average molecular weight of such materials can vary widely, but will typically be up to about 500, preferably from about 200 to about 400, and more preferably from about 300 to about 350. Also useful herein are the various grades of mineral oils. Mineral oils are liquid mixtures of hydrocarbons that are obtained from petroleum. Specific examples of suitable hydrocarbon materials include paraffin oil, mineral oil, dodecane, isododecane, hexadecane, isohexadecane, eicosene, isoeicosene, tridecane, tetradecane, polybutene, polyisobutene, and mixtures thereof. Preferred for use herein are hydrocarbons selected from the group consisting of mineral oil, poly α -olefin oils such as isododecane, isohexadecane, polybutene, polyisobutene, and mixtures thereof.

Commercially available fatty alcohols and their derivatives useful herein

include: oleyl alcohol with tradename UNJECOL 90BHR available from Shin Nihon Rika, various liquid esters with tradenames SCHERCEMOL series available from Scher, and hexyl isostearate with a tradename HIS and isopropyl isostearate having a tradename ZPIS available from Kokyu Alcohol.

5 Commercially available bulky ester oils useful herein include: trimethylolpropane tricaprilate/tricaprate with tradename MOBIL ESTER P43 from Mobil Chemical Co. Commercially available hydrocarbons useful herein include isododecane, isohexadecane, and isoeicosene with tradenames PERMETHYL 99A, PERMETHYL 101A, and PERMETHYL 1082, available from Presperse (South

10 Plainfield New Jersey, USA), a copolymer of isobutene and normal butene with tradenames INDOPOL H-100 available from Amoco Chemicals (Chicago Illinois, and USA), mineral oil with tradename BENOL available from Witco, isoparaffin with tradename ISOPAR from Exxon Chemical Co. (Houston Texas, USA.)

The compositions of the present invention are transparent. What is meant

15 by transparent, is that a black substance having the size of a 1cm X 1cm square can be detected by the naked eye through 1cm thickness of the present composition.

SILICONE COMPOUND

The compositions of the present invention may further comprise a silicone

20 compound. The silicone compounds useful herein include volatile soluble or insoluble, or nonvolatile soluble or insoluble silicone conditioning agents. By soluble what is meant is that the silicone compound is miscible with the carrier of the composition so as to form part of the same phase. By insoluble what is meant is that the silicone forms a separate, discontinuous phase from the carrier,

25 such as in the form of an emulsion or a suspension of droplets of the silicone. The silicone compounds herein may be made by any suitable method known in the art, including emulsion polymerization. The silicone compounds may further be incorporated in the present composition in the form of an emulsion, wherein the emulsion is made by mechanical mixing, or in the stage of synthesis through

30 emulsion polymerization, with or without the aid of a surfactant selected from anionic surfactants, nonionic surfactants, cationic surfactants, and mixtures thereof.

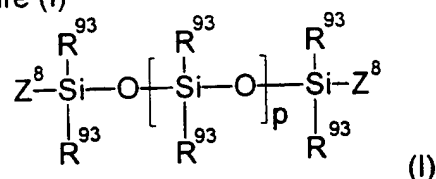
The silicone compounds for use herein will preferably have a viscosity of from about 1,000 to about 2,000,000 centistokes at 25°C, more preferably from

35 about 10,000 to about 1,800,000, and even more preferably from about 100,000

to about 1,500,000. The viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970. Silicone compound of high molecular weight may be made by emulsion polymerization. Suitable silicone fluids include polyalkyl
 5 siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other nonvolatile silicone compounds having hair conditioning properties can also be used.

The silicone compounds herein are preferably used at levels by weight of the composition of from about 0.1% to about 60%, more preferably from about
 10 0.1% to about 40%.

The silicone compounds herein also include polyalkyl or polyaryl siloxanes with the following structure (I)



wherein R^{93} is alkyl or aryl, and x is an integer from about 7 to about 8,000. Z^8
 15 represents groups which block the ends of the silicone chains. The alkyl or aryl groups substituted on the siloxane chain (R^{93}) or at the ends of the siloxane chains Z^8 can have any structure as long as the resulting silicone remains fluid at room temperature, is dispersible, is neither irritating, toxic nor otherwise harmful when applied to the hair, is compatible with the other components of the
 20 composition, is chemically stable under normal use and storage conditions, and is capable of being deposited on and conditions the hair. Suitable Z^8 groups include hydroxy, methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R^{93} groups on the silicon atom may represent the same group or different groups. Preferably, the two R^{93} groups represent the same group. Suitable R^{93} groups
 25 include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicone compounds are polydimethylsiloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane, which is also known as dimethicone, is especially preferred. The polyalkylsiloxanes that can be used include, for example, polydimethylsiloxanes. These silicone compounds are
 30 available, for example, from the General Electric Company in their Viscasil® and SF 96 series, and from Dow Corning in their Dow Corning 200 series.

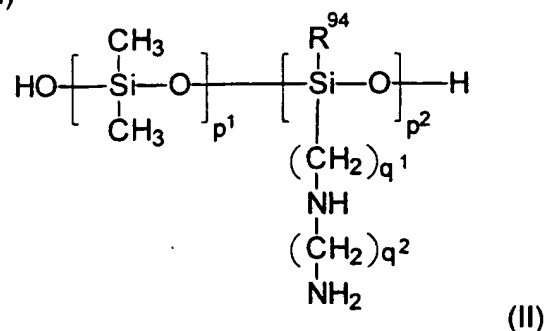
Polyalkylaryl siloxane fluids can also be used and include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from

the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

Especially preferred, for enhancing the shine characteristics of hair, are highly arylated silicone compounds, such as highly phenylated polyethyl silicone having refractive index of about 1.46 or higher, especially about 1.52 or higher. When these high refractive index silicone compounds are used, they should be mixed with a spreading agent, such as a surfactant or a silicone resin, as described below to decrease the surface tension and enhance the film forming ability of the material.

The silicone compounds that can be used include, for example, a polypropylene oxide modified polydimethylsiloxane although ethylene oxide or mixtures of ethylene oxide and propylene oxide can also be used. The ethylene oxide and polypropylene oxide level should be sufficiently low so as not to interfere with the dispersibility characteristics of the silicone. These material are also known as dimethicone copolyols.

Other silicone compounds include amino substituted materials. Suitable alkylamino substituted silicone compounds include those represented by the following structure (II)



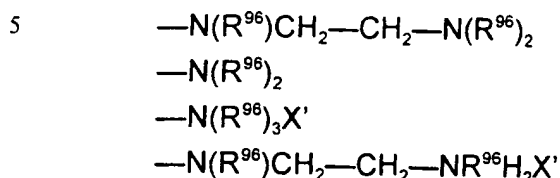
wherein R^{94} is H, CH_3 or OH, p^1 , p^2 , q^1 and q^2 are integers which depend on the molecular weight, the average molecular weight being approximately between 5,000 and 10,000. This polymer is also known as "amodimethicone".

Suitable amino substituted silicone fluids include those represented by the formula (III)



in which G is chosen from the group consisting of hydrogen, phenyl, OH, C_1 - C_8 alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably equals 0; b denotes 0 or 1 and preferably equals 1; the sum p^3+p^4 is a number from 1 to 2,000 and preferably from 50 to 150, p^3 being able to denote a number

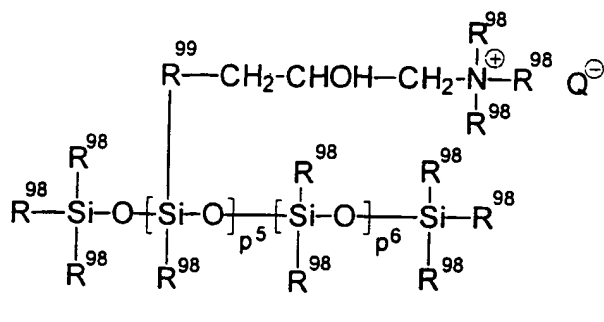
from 0 to 1,999 and preferably from 49 to 149 and p^4 being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R^{97} is a monovalent radical of formula $C_{q^3}H_{2q^3}L$ in which q^3 is an integer from 2 to 8 and L is chosen from the groups



in which R^{96} is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and X' denotes a halide ion.

An especially preferred amino substituted silicone corresponding to formula (II) is the polymer known as "trimethylsilylamodimethicone" wherein R^{94} is CH_3 .

Other amino substituted silicone polymers which can be used are represented by the formula (V):



where R^{98} denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, preferably an alkyl or alkenyl radical such as methyl; R^{99} denotes a hydrocarbon radical, preferably a $\text{C}_1\text{--C}_{18}$ alkylene radical or a $\text{C}_1\text{--C}_{18}$, and more preferably $\text{C}_1\text{--C}_8$, alkyleneoxy radical; Q^- is a halide ion, preferably chloride; p^5 denotes an average statistical value from 2 to 20, preferably from 2 to 8; p^6 denotes an average statistical value from 20 to 200, and preferably from 20 to 50. A preferred polymer of this class is available from Union Carbide under the name "UCAR SILICONE ALE 56".

References disclosing suitable nonvolatile dispersed silicone compounds include U.S. Patent No. 2,826,551, to Geen; U.S. Patent No. 3,964,500, to Drakoff, issued June 22, 1976; U.S. Patent No. 4,364,837, to Pader; and British Patent No. 849,433, to Woolston. "Silicon Compounds" distributed by Petrarch

Systems, Inc., 1984, provides an extensive, though not exclusive, listing of suitable silicone compounds.

Another nonvolatile dispersed silicone that can be especially useful is a silicone gum. The term "silicone gum", as used herein, means a polyorganosiloxane material having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. It is recognized that the silicone gums described herein can also have some overlap with the above-disclosed silicone compounds. This overlap is not intended as a limitation on any of these materials. Silicone gums are described by Petrarch, and others including U.S. Patent No. 4,152,416, to Spitzer *et al.*, issued May 1, 1979 and Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000. Specific examples include polydimethylsiloxane, poly(dimethylsiloxane methylvinylsiloxane) copolymer, poly(dimethylsiloxane diphenylsiloxane methylvinylsiloxane) copolymer and mixtures thereof.

Also useful are silicone resins, which are highly crosslinked polymeric siloxane systems. The crosslinking is introduced through the incorporation of tri-functional and tetra-functional silanes with mono-functional or di-functional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units, and hence, a sufficient level of crosslinking, such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinylchlorosilanes, and tetrachlorosilane, with the methyl substituted silanes being most commonly utilized. Preferred resins are offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will

generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art. Without being bound by theory, it is
5 believed that the silicone resins can enhance deposition of other silicone compounds on the hair and can enhance the glossiness of hair with high refractive index volumes.

Other useful silicone resins are silicone resin powders such as the material given the CTFA designation polymethylsilsequioxane, which is
10 commercially available as Tospearl™ from Toshiba Silicones.

The method of manufacturing these silicone compounds, can be found in Encyclopedia of Polymer Science and Engineering, Volume 15, Second Edition, pp. 204-308, John Wiley & Sons, Inc., 1989.

Silicone materials and silicone resins in particular, can conveniently be
15 identified according to a shorthand nomenclature system well known to those skilled in the art as the "MDTQ" nomenclature. Under this system, the silicone is described according to the presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the mono-functional unit $(\text{CH}_3)_3\text{SiO}_{0.5}$; D denotes the difunctional unit $(\text{CH}_3)_2\text{SiO}$; T denotes the
20 trifunctional unit $(\text{CH}_3)\text{SiO}_{1.5}$; and Q denotes the quadri- or tetra-functional unit SiO_2 . Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyl, amino, hydroxyl, etc. The molar ratios of the various units, either in terms of subscripts to the symbols
25 indicating the total number of each type of unit in the silicone, or an average thereof, or as specifically indicated ratios in combination with molecular weight, complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before,
30 however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, MQ and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to
35 about 1.5:1.0 and the average molecular weight of the resin is from about 1000

to about 10,000.

Particularly suitable silicone compounds herein are non-volatile silicone oils having a molecular weight of from about 200,000 to about 600,000 such as Dimethicone, and Dimethiconol. These silicone compounds can be incorporated
5 in the composition as silicone oils solutions; the silicone oils being volatile or non-volatile.

Commercially available silicone compounds which are useful herein include Dimethicone with tradename DC345 available from Dow Corning Corporation, Dimethicone gum solutions with tradenames SE 30, SE 33, SE 54
10 and SE 76 available from General Electric, Dimethiconol with tradenames DCQ2-1403 and DCQ2-1401 available from Dow Corning Corporation, and emulsion polymerized Dimethiconol available from Toshiba Silicone as described in GB application 2,303,857.

HUMECTANT

15 The compositions of the present invention may further comprise a humectant. The humectants herein are selected from the group consisting of polyhydric alcohols, water soluble alkoxyated nonionic polymers, and mixtures thereof. The humectants herein are preferably used at levels by weight of the composition of from about 0.1% to about 20%, more preferably from about 0.5%
20 to about 5%.

Polyhydric alcohols useful herein include glycerin, sorbitol, propylene glycol, butylene glycol, hexylene glycol, ethoxylated glucose, 1, 2-hexane diol, hexanetriol, dipropylene glycol, erythritol, trehalose, diglycerin, xylitol, maltitol, maltose, glucose, fructose, sodium chondroitin sulfate, sodium hyaluronate,
25 sodium adenosin phosphate, sodium lactate, pyrrolidone carbonate, glucosamine, cyclodextrin, and mixtures thereof.

Water soluble alkoxyated nonionic polymers useful herein include polyethylene glycols and polypropylene glycols having a molecular weight of up to about 1000 such as those with CTFA names PEG-200, PEG-400, PEG-600,
30 PEG-1000, and mixtures thereof.

Commercially available humectants herein include: glycerin with tradenames STAR and SUPEROL available from The Procter & Gamble Company, CRODEROL GA7000 available from Croda Universal Ltd., PRECERIN series available from Unichema, and a same tradename as the
35 chemical name available from NOF; propylene glycol with tradename LEXOL

PG-865/855 available from Inolex, 1,2-PROPYLENE GLYCOL USP available from BASF; sorbitol with tradenames LIPONIC series available from Lipo, SORBO, ALEX, A-625, and A-641 available from ICI, and UNISWEET 70, UNISWEET CONC available from UPI; dipropylene glycol with the same
5 tradename available from BASF; diglycerin with tradename DIGLYCEROL available from Solvay GmbH; xylitol with the same tradename available from Kyowa and Eizai; maltitol with tradename MALBIT available from Hayashibara, sodium chondroitin sulfate with the same tradename available from Freeman and Bioiberica, and with tradename ATOMERGIC SODIUM CHONDROITIN
10 SULFATE available from Atomergic Chemetals; sodium hyaluronate with tradenames ACTIMOIST available from Active Organics, AVIAN SODIUM HYALURONATE series available from Intergen, HYALURONIC ACID Na available from Ichimaru Pharcos; sodium adenosin phosphate with the same tradename available from Asahikasei, Kyowa, and Daiichi Seiyaku; sodium
15 lactate with the same tradename available from Merck, Wako, and Showa Kako, cyclodextrin with tradenames CAVITRON available from American Maize, RHODOCAP series available from Rhone-Poulenc, and DEXPEARL available from Tomen; and polyethylene glycols with the tradename CARBOWAX series available from Union Carbide.

20 ADDITIONAL CONDITIONING AGENT

The compositions of the present invention may further comprise an additional conditioning agent selected from the group consisting of amphoteric conditioning polymers, high melting point compounds, high molecular weight ester oils, and mixtures thereof. Additional conditioning agents are selected
25 according to the compatibility with other components, and the desired characteristic of the product. The additional conditioning agents herein are preferably used at levels by weight of the composition of from about 0.01% to about 10%.

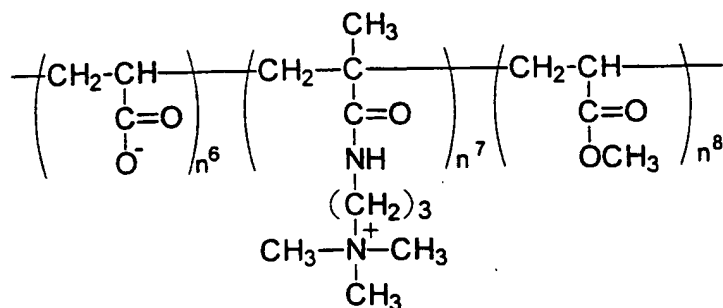
Amphoteric Conditioning Polymer

30 The compositions of the present invention comprise an amphoteric conditioning polymer. The amphoteric conditioning polymers herein are those compatible with the carboxylic acid/carboxylate copolymers and which provide conditioning benefit to the hair. Although some of the amphoteric conditioning polymers herein may have some hair holding or hair fixative properties, such hair
35 holding or hair fixative properties are not a requirement for the amphoteric

conditioning polymers herein. The amphoteric conditioning polymers useful herein are those including at least one cationic monomer and at least one anionic monomer; the cationic monomer being quaternary ammonium, preferably dialkyl diallyl ammonium chloride or carboxylamidoalkyl trialkyl ammonium chloride; and
 5 the anionic monomer being carboxylic acid. The amphoteric conditioning polymers herein may include nonionic monomers such as acrylamine, methacrylate, or ethacrylate. Further, the amphoteric conditioning polymers useful herein do not contain betanized monomers.

The composition of the present invention preferably comprises the
 10 amphoteric conditioning polymer at a level by weight of from about 0.01% to about 10%, more preferably from about 0.1% to about 5%.

Useful herein are polymers with the CTFA name Polyquaternium 22, Polyquaternium 39, and Polyquaternium 47. Such polymers are, for example, copolymers consisting of dimethyldiallyl ammonium chloride and acrylic acid,
 15 terpolymers consisting of dimethyldiallyl ammonium chloride and acrylamide, and terpolymers consisting of acrylic acid methacrylamidopropyl trimethylammonium chloride and methyl acrylate such as those of the following formula wherein the ratio of $n^6:n^7:n^8$ is 45:45:10:



20

Highly preferred commercially available amphoteric conditioning polymers herein include Polyquaternium 22 with tradenames MERQUAT 280, MERQUAT 295, Polyquaternium 39 with tradenames MERQUAT PLUS 3330, MERQUAT
 25 PLUS 3331, and Polyquaternium 47 with tradenames MERQUAT 2001, MERQUAT 2001N, all available from Calgon Corporation.

Also useful herein are polymers resulting from the copolymerisation of a vinyl monomer carrying at least one carboxyl group, such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, fumaric acid, crotonic acid, or

alphachloroacrylic acid, and a basic monomer which is a substituted vinyl compound containing at least one basic nitrogen atom, such as dialkylaminoalkyl methacrylates and acrylates and dialkylaminoalkylmethacrylamides and acrylamides.

5 Also useful herein are polymers containing units derived from:

- i) at least one monomer chosen from amongst acrylamides or methacrylamides substituted on the nitrogen by an alkyl radical,
- ii) at least one acid comonomer containing one or more reactive carboxyl groups, and
- 10 iii) at least one basic comonomer, such as esters, with primary, secondary and tertiary amine substituents and quaternary ammonium substituents, of acrylic and methacrylic acids, and the product resulting from the quaternisation of dimethylaminoethyl methacrylate with dimethyl or diethyl sulfate.

15 The N-substituted acrylamides or methacrylamides which are most particularly preferred are the groups in which the alkyl radicals contain from 2 to 12 carbon atoms, especially N-ethylacrylamide, N-tert.-butylacrylamide, N-tert.-octylacrylamide, N-octylacrylamide, N-decylacrylamide and N-dodecylacrylamide and also the corresponding methacrylamides. The acid comonomers are chosen
20 more particularly from amongst acrylic, methacrylic, crotonic, itaconic, maleic and fumaric acids and also the alkyl monoesters of maleic acid or fumaric acid in which alkyl has 1 to 4 carbon atoms.

The preferred basic comonomers are aminoethyl, butylaminoethyl, N,N'-dimethylaminoethyl and N-tert.-butylaminoethyl methacrylates.

25 Commercially available amphoteric conditioning polymers herein include octylacrylamine/acrylates/butylaminoethyl methacrylate copolymers with the tradenames AMPHOMER, AMPHOMER SH701, AMPHOMER 28-4910, AMPHOMER LV71, and AMPHOMER LV47 supplied by National Starch & Chemical.

30 High Melting Point Compound

The high melting point compound useful herein have a melting point of at least about 25°C selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, hydrocarbons, steroids, and mixtures thereof. It is understood by the artisan that the compounds disclosed in
35 this section of the specification can in some instances fall into more than one

classification, e.g., some fatty alcohol derivatives can also be classified as fatty acid derivatives. However, a given classification is not intended to be a limitation on that particular compound, but is done so for convenience of classification and nomenclature. Further, it is understood by the artisan that, depending on the number and position of double bonds, and length and position of the branches, certain compounds having certain required carbon atoms may have a melting point of less than about 25°C. Such compounds of low melting point are not intended to be included in this section. Nonlimiting examples of the high melting point compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992.

It is believed that these high melting point compounds cover the hair surface and reduce friction, thereby resulting in providing smooth feel on the hair and ease of combing.

The fatty alcohols useful herein are those having from about 14 to about 30 carbon atoms, preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated. Nonlimiting examples of fatty alcohols include, cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof.

The fatty acids useful herein are those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Also included are diacids, triacids, and other multiple acids which meet the requirements herein. Also included herein are salts of these fatty acids. Nonlimiting examples of fatty acids include lauric acid, palmitic acid, stearic acid, behenic acid, sebacic acid, and mixtures thereof.

The fatty alcohol derivatives and fatty acid derivatives useful herein include alkyl ethers of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, esters of fatty alcohols, fatty acid esters of compounds having esterifiable hydroxy groups, hydroxy-substituted fatty acids, and mixtures thereof. Nonlimiting examples of fatty alcohol derivatives and fatty acid derivatives include materials such as methyl stearyl ether; the ceteth series of compounds such as ceteth-1 through ceteth-45, which are ethylene glycol ethers of cetyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; the steareth series of compounds such as

steareth-1 through 10, which are ethylene glycol ethers of steareth alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; cetareth 1 through cetareth-10, which are the ethylene glycol ethers of cetareth alcohol, *i.e.* a mixture of fatty alcohols containing predominantly cetyl and stearyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; C₁-C₃₀ alkyl ethers of the ceteth, steareth, and cetareth compounds just described; polyoxyethylene ethers of behenyl alcohol; ethyl stearate, cetyl stearate, cetyl palmitate, stearyl stearate, myristyl myristate, polyoxyethylene cetyl ether stearate, polyoxyethylene stearyl ether stearate, polyoxyethylene lauryl ether stearate, ethyleneglycol monostearate, polyoxyethylene monostearate, polyoxyethylene distearate, propyleneglycol monostearate, propyleneglycol distearate, trimethylolpropane distearate, sorbitan stearate, polyglyceryl stearate, glyceryl monostearate, glyceryl distearate, glyceryl tristearate, and mixtures thereof.

Hydrocarbons useful herein include compounds having at least about 20 carbons.

Steroids useful herein include compounds such as cholesterol.

High melting point compounds of a single compound of high purity are preferred. Single compounds of pure fatty alcohols selected from the group of pure cetyl alcohol, stearyl alcohol, and behenyl alcohol are highly preferred. By "pure" herein, what is meant is that the compound has a purity of at least about 90%, preferably at least about 95%. These single compounds of high purity provide good rinsability from the hair when the consumer rinses off the composition.

Commercially available high melting point compounds useful herein include: cetyl alcohol, stearyl alcohol, and behenyl alcohol having tradenames KONOL series available from Shin Nihon Rika (Osaka, Japan), and NAA series available from NOF (Tokyo, Japan); pure behenyl alcohol having tradename 1-DOCOSANOL available from WAKO (Osaka, Japan), various fatty acids having tradenames NEO-FAT available from Akzo (Chicago Illinois, USA), HYSTRENE available from Witco Corp. (Dublin Ohio, USA), and DERMA available from Vevy (Genova, Italy); and cholesterol having tradename NIKKOL AGUASOME LA available from Nikko.

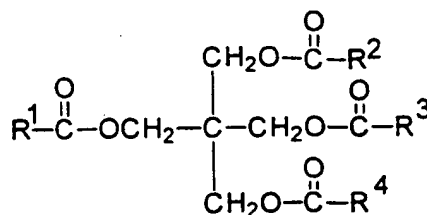
High Molecular Weight Ester Oils

High molecular weight ester oils are useful herein. The high molecular

weight ester oils useful herein are those which are water insoluble, have a molecular weight of at least about 500, preferably at least about 800, and are in liquid form at 25°C. Useful high molecular weight ester oils herein include pentaerythritol ester oils, trimethylol ester oils, poly α -olefin oils, citrate ester oils, glyceryl ester oils, and mixtures thereof. As used herein, the term "water insoluble" means the compound is substantially not soluble in water at 25°C; when the compound is mixed with water at a concentration by weight of above 1.0%, preferably at above 0.5%, the compound is temporarily dispersed to form an unstable colloid in water, then is quickly separated from water into two phases.

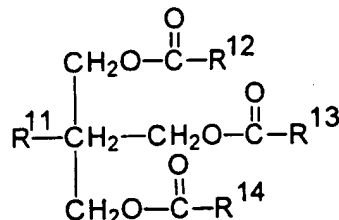
The high molecular weight ester oil herein provides conditioning benefits such as moisturized feel, smooth feel, and manageability control to the hair when the hair is dried, yet not leave the hair feeling greasy. It is believed that water insoluble oily material in general are capable of being deposited on the hair. Without being bound by theory, it is believed that, because of its bulkiness, the high molecular weight ester oil covers the surface of the hair and, as a result, the high molecular weight ester oil reduces hair friction to deliver smoothness and manageability control to the hair. It is also believed that, because it has some hydrophilic groups, the high molecular weight ester oil provides moisturized feel, yet, because it is liquid, does not leave the hair feeling greasy. The high molecular weight ester oil is chemically stable under normal use and storage conditions.

Pentaerythritol ester oils useful herein are those having the following formula:



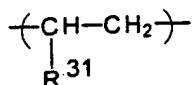
wherein R^1 , R^2 , R^3 , and R^4 , independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons. Preferably, R^1 , R^2 , R^3 , and R^4 , independently, are branched, straight, saturated, or unsaturated alkyl groups having from about 8 to about 22 carbons. More preferably, R^1 , R^2 , R^3 and R^4 are defined so that the molecular weight of the compound is from about 800 to about 1200.

Trimethylol ester oils useful herein are those having the following formula:



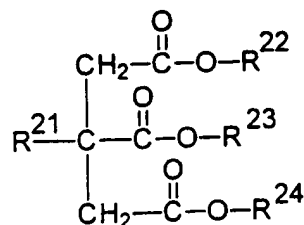
wherein R^{11} is an alkyl group having from 1 to about 30 carbons, and R^{12} , R^{13} , and R^{14} , independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons. Preferably, R^{11} is ethyl and R^{12} , R^{13} , and R^{14} , independently, are branched, straight, saturated, or unsaturated alkyl groups having from 8 to about 22 carbons. More preferably, R^{11} , R^{12} , R^{13} and R^{14} are defined so that the molecular weight of the compound is from about 800 to about 1200.

Poly α -olefin oils useful herein are those having the following formula and having a viscosity of from about 1 to about 35,000 cst, a molecular weight of from about 200 to about 60,000, and a polydispersity of no more than about 3;



wherein R^{31} is an alkyl having from about 4 to 14 carbons, preferably 4 to 10 carbons. Poly α -olefin oils having a molecular weight of at least about 800 are useful herein. Such high molecular weight poly α -olefin oils are believed to provide long lasting moisturized feel to the hair. Poly α -olefin oils having a molecular weight of less than about 800 are useful herein. Such low molecular weight poly α -olefin oils are believed to provide a smooth, light, clean feel to the hair.

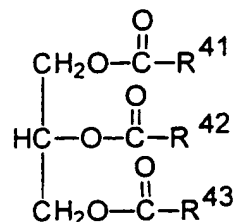
Citrate ester oils useful herein are those having a molecular weight of at least about 500 having the following formula:



wherein R^{21} is OH or CH_3COO , and R^{22} , R^{23} , and R^{24} , independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups

having from 1 to about 30 carbons. Preferably, R²¹ is OH, and R²², R²³, and R²⁴, independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 8 to about 22 carbons. More preferably, R²¹, R²², R²³ and R²⁴ are defined so that the molecular weight of the compound is at least about 800.

Glycerol ester oils useful herein are those having a molecular weight of at least about 500 and having the following formula:



wherein R⁴¹, R⁴², and R⁴³, independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons. Preferably, R⁴¹, R⁴², and R⁴³, independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 8 to about 22 carbons. More preferably, R⁴¹, R⁴², and R⁴³ are defined so that the molecular weight of the compound is at least about 800.

Particularly useful pentaerythritol ester oils and trimethylol ester oils herein include pentaerythritol tetraistearate, pentaerythritol tetraoleate, trimethylolpropane triistearate, trimethylolpropane trioleate, and mixtures thereof. Such compounds are available from Kokyo Alcohol with tradenames KAKPTI, KAKTTI, and Shin-nihon Rika with tradenames PTO, ENUJERUBU TP3SO.

Particularly useful poly α -olefin oils herein include polydecenes with tradenames PURESYN 6 having a number average molecular weight of about 500 and PURESYN 100 having a number average molecular weight of about 3000 and PURESYN 300 having a number average molecular weight of about 6000 available from Mobil Chemical Co.

Particularly useful citrate ester oils herein include triisocetyl citrate with tradename CITMOL 316 available from Bernel, triisostearyl citrate with tradename PELEMOL TISC available from Phoenix, and trioctyldecyl citrate with tradename CITMOL 320 available from Bernel.

Particularly useful glycerol ester oils herein include triistearin with tradename SUN ESPOL G-318 available from Taiyo Kagaku, triolein with

tradename CITHROL GTO available from Croda Surfactants Ltd., trilinolein with tradename EFADERMA-F available from Vevy, or tradename EFA-GLYCERIDES from Brooks.

Other Additional Components

5 The compositions of the present invention may include other additional components, which may be selected by the artisan according to the desired characteristics of the final product and which are suitable for rendering the composition more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. Such other additional components generally are
10 used individually at levels of from about 0.001% to about 10%, preferably up to about 5% by weight of the composition.

A wide variety of other additional components can be formulated into the present compositions. These include: other conditioning agents such as hydrolysed collagen with tradename Pepten 2000 available from Hormel, vitamin
15 E with tradename Emix-d available from Eisai, panthenol available from Roche, panthenyl ethyl ether available from Roche, hydrolysed keratin, proteins, plant extracts, and nutrients; hair-fixative polymers such as amphoteric fixative polymers, cationic fixative polymers, anionic fixative polymers, nonionic fixative polymers, and silicone grafted copolymers; preservatives such as benzyl alcohol,
20 methyl paraben, propyl paraben and imidazolidinyl urea; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and
25 persulfate salts; hair reducing agents such as the thioglycolates; perfumes; and sequestering agents, such as disodium ethylenediamine tetra-acetate; ultraviolet and infrared screening and absorbing agents such as octyl salicylate, antidandruff agents such as zinc pyrithione; and mixtures thereof.

EXAMPLES

30 The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the
35 spirit and scope of the invention. Ingredients are identified by chemical or CTFA

name, or otherwise defined below.

The compositions of the present invention are suitable for making products in the form of emulsion, cream, gel, spray or, mousse, and are particularly used for leave-on products in the form of gel. The products can be used on wet hair or dried hair.

Compositions

Components	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Sorbitan monooleate	-	-	-	-	-	5.0
Diglyceryl diloeate	-	-	15.0	-	-	-
PEG-10 hydrogenated castor oil	-	-	-	10.0	-	-
Dimethicone copolyol 1 *1	-	-	-	-	10.0	-
Dimethicone copolyol 2 *2	-	-	-	-	-	5.0
Acrylic acid/alkyl acrylate cross copolymer 1 *3	1.0	1.5	1.5	-	-	0.5
Triethanolamine *4	0.8	1.2	1.2	-	-	0.4
Breakable visible particle 1 *5	0.1	-	-	-	0.2	0.1
Breakable visible particle 2 *6	-	0.2	-	0.1	-	-
Breakable visible particle 3 *7	-	-	0.1	0.1	-	0.1
JoJoba Oil *8	-	20.0	-	40.0	-	10.0
Mineral Oil *9	20.0	20.0	15.0	15.0	10.0	5.0
Trimethylolpropane tricaprylate/tricaprate*10	-	10.0	10.0	-	-	10.0
Pentaerythritol Tetraoleate *11	-	-	-	-	5.0	5.0
Cyclomethicone/Dimethiconol *12	10.0	-	10.0	-	10.0	-
Cyclomethicone *13	-	10.0	10.0	10.0	-	10.0
Dimethicone/Dimethiconol *14	10.0	-	-	-	-	5.0
PEG-4 *15	15.0	-	-	10.0	-	10.0
Hexylene Glycol	10.0	10.0	-	-	10.0	-
Vitamin E *16	0.2	-	-	0.2	-	-
Panthenol *17	-	-	-	-	-	0.2
Camphor *18	-	0.2	-	-	-	-
Ethanol	25.0	-	20.0	5.0	-	-
Methyl paraben	0.2	0.2	0.2	0.2	0.2	0.2
Phenoxyethanol	0.2	0.2	0.2	0.2	0.2	0.2
Sodium Salt	-	-	-	-	0.1	0.2

Perfume	0.1	0.1	0.1	0.1	0.1	0.1
Deionized Water	----- q.s. to 100% -----					

Definitions of Components

- *1 Dimethicone copolyol 1: SH3772C available from Dow Corning
- *2 Dimethicone copolyol 2: SH3748 available from Dow Corning
- *3 Acrylic acid/alkyl acrylate copolymer: PEMULEN TR-2 available from
5 B.F. Goodrich
- *4 Triethanolamine: Triethanolamine available from Nippon Shokubai
- *5 Breakable visible particle 1: Unispheres AGE-527 available from Induchem
AG
- *6 Breakable visible particle 2: Unispheres YE-501: available from Induchem
10 AG
- *7 Breakable visible particle 3: Unicerin C-30 available from Induchem AG
- *8 Jojoba oil: jojoba oil available from Nikko Chemical
- *9 Mineral oil: BENOL available from Witico
- *10 Trimethylolpropane tricaprylate/tricaprate: MOBIL ESTER P14 available
15 from Mobil Chemical
- *11 Pentaerythritol Tetraoleate: Pentaerythritol Tetraoleate Available from Shin-
Nihon Rika
- *12 Cyclomethicone/Dimethiconol: Dow Corning Q2-1401 available from Dow
Corning
- 20 *13 Cyclomethicone: Dow Corning 345 available from Dow Corning
- *14 Dimethicone/Dimethiconol: Dow Corning Q2-1403 available from Dow
Corning
- *15 PEG-4: Carbowax PEG200 available from Union Carbide
- *16 Vitamin E: Emix-d obtained by Eisai.
- 25 *17 Panthenol: Available from Roche.
- *18 Camphor: Camphor available from American Hoechst Corp.

Method of Preparation

The hair conditioning products of Examples 1 through 6 are suitably made
as follows: oils for the carrier, hydrophobic emulsifier, and high molecular weight
30 ester oils and silicone compounds, if included, are mixed until homogenous. To
this is added the breakable visible particles and mixed with vigorous agitation to
make a first premix. In a separate container, the remaining components are
dissolved in water and/or ethanol to make a second premix. The first and second

premises are blended with agitation until homogenous. A triblender can be used as necessary to disperse the components.

5 Examples 1 through 6 are hair conditioning compositions of the present invention which are particularly useful for leave-on use. These examples have many advantages. For example, they are transparent and show the breakable visible particles distinctively. They can further provide improved conditioning benefits to the hair such as smoothness, softness, and reduction of friction, and are easy to apply on the hair. The breakable visible particles readily disintegrate with little shear on the hand with the fingers.

10

It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from its spirit and scope.

WHAT IS CLAIMED IS:

1. A hair conditioning composition comprising:
 - 5 (1) a hydrophobic emulsifier selected from the group consisting of carboxylic acid/carboxylate copolymer, nonionic surfactant having an HLB of from about 1 to about 10, silicone derivative surfactant, and mixtures thereof;
 - (2) a breakable visible particle comprising structural material selected from the group consisting of polysaccharides and their derivatives, saccharides and their derivatives, oligosaccharides, monosaccharides, and mixtures
10 thereof; and
 - (3) an oily continuous phase carrier;wherein the composition is transparent.
2. The hair conditioning composition according to Claim 1 wherein the nonionic surfactant has an HLB of from about 3 to about 8.
3. The hair conditioning composition according to Claim 1 or 2 further comprising a silicone compound.
4. The hair conditioning composition according to any of the preceding claims further comprising a humectant.

INTERNATIONAL SEARCH REPORT

Inte: onal Application No

PCT/US 99/00012

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/06 A61K7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 316 054 A (SHISEIDO CO LTD) 17 May 1989 (1989-05-17) claims 1-11; examples 6-5 ---	1,2
A	EP 0 590 538 A (CURTIS HELENE IND INC) 6 April 1994 (1994-04-06) page 4, line 56 - line 58 page 9, line 29 - line 31 claims 1,12,15,17; example 4 ---	1,3,4
A	WO 97 23194 A (CHEIL JEDANG CORP ;KANG GIL SUNG (KR); KIM IN HO (KR); PARK HAE HO) 3 July 1997 (1997-07-03)	1,2
X	comparative ex.1 page 9, line 4 - line 25 claims; examples --- -/--	1,3,4

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

9 September 1999

Date of mailing of the international search report

23/09/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Loiselet-Taisne, S

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/00012

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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